

**Synthesis, Characterization and Kinetic Investigations of Heterophase Materials
Prepared Using Group Transfer Polymerization**

by

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**SYNTHESIS, CHARACTERIZATION, AND KINETIC INVESTIGATIONS
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(ABSTRACT)

The impact of multiphase polymeric materials has been enhanced by the preparation of well defined block and graft copolymers. Hence, there has been a growing emphasis on new synthetic methods for the preparation of blocks and grafts. Group Transfer Polymerization (GTP) is a relatively new synthetic method which provides a means to obtain poly(alkyl acrylate)s and poly(alkyl methacrylate)s via a "living" mechanism over a broad temperature range. The degree of control over molecular weight and molecular weight distribution rivals that afforded through living anionic techniques for the preparation of poly(alkyl methacrylate)s.

The objectives of this research were many fold. The first was to establish GTP as a routine synthetic tool for the preparation of poly(alkyl methacrylate)s in our

laboratories. This involved utilizing a variety of initiators, catalysts and alkyl methacrylate monomers. Furthermore, kinetic studies of the GTP of MMA with a controlled temperature, "living" polymerization reactor and tetrabutylammonium benzoate as the selected catalyst were initiated. These investigations involved the determination of the reaction order with respect to initiator and catalyst concentrations. Also, the global energy of activation, under controlled reaction conditions, was elucidated.

To extend the synthetic utility of GTP, novel block and graft copolymers were synthesized. Transformation reactions and the macromonomer technique to interrelate different synthetic routes further extends the range of block and graft copolymers which can be prepared. Poly(dimethylsiloxane) (PDMS) macromers were prepared via the anionic ring opening polymerization of hexamethylcyclotrisiloxane, which is subsequently terminated with a chlorosilane derivative of allyl methacrylate. The macromonomer technique has been employed to synthesize poly(methylmethacrylate)-g-poly(dimethylsiloxane) copolymers of controlled molecular weight and apparent narrow molecular weight distribution by GPC. Transformation of the methacrylate functional group on the PDMS provided a suitable macroinitiator for the GTP of methyl methacrylate, which leads to siloxane-b-methacrylate copolymers via a novel route.

Dedicated to

Mom and Dad, who have always known
the right things to say and who have given
their love and support in so many different ways.

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"Silent gratitude isn't much use to anyone"

G.B.Stern

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Though I have had the opportunity to work and come to know these colleagues, I have never worked closer or harder with anyone than with I owe
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taught me, the expression of technical insight and value of discussions clearly stands out.

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CHAPTER I**INTRODUCTION**

Traditionally, polymers of α,β -unsaturated esters have been prepared via anionic and free radical techniques. Prior to 1984 these were also the techniques utilized in our laboratories for the preparation of polymers having methacrylic ester components. With the discovery of GTP by investigators at duPont it was of interest to examine this mechanism for the preparation of alkyl methacrylate containing homopolymers and copolymers.

Initial investigations focused on the development of a methodology for the preparation of homopolymers having controlled molecular weight and narrow molecular weight distributions. Thus, the primary focus centered on meeting the purity requirements of reagents; solvents, monomers, initiators and catalysts, which would permit (on a laboratory scale) the preparation of polymers of controlled molecular weights. The living nature of the mechanism was

further demonstrated by the preparation of all-methacrylic ester block copolymers and well-defined "chelic" homopolymers based on PMMA.

Fundamental investigations into kinetic aspects of the process were initiated to gain more insight into the polymerization mechanism. This work entailed investigations of the GTP of MMA in the presence of dimethyl(methyl-trimethylsilyl)ketene acetal (MTS) as the initiator and tetrabutylammonium benzoate (TBAB) as the selected catalyst. The benzoate catalyst is also soluble in the polymerization solvent, THF, unlike some of the previously reported fluoride catalysts used in GTP. It was of interest to gain more insight into the activity and role of the benzoate system since it was the catalyst of choice for the GTP polymerization of multicomponent systems containing poly(dimethylsiloxane) (PDMS). It was possible to explore the effect of both the benzoate catalyst and initiator concentrations on the rate of polymerization while maintaining strict temperature control by employing a low pressure "living" polymerization reactor. It appears that the rate may be significantly influenced by both the concentration of catalyst and molar ratio of initiator to catalyst. A value for the global energy of activation was determined for a specific catalyst level with this reactor system.

INTRODUCTION

In addition to these fundamental investigations, research was directed toward the preparation of well-defined copolymers containing PDMS. Siloxane block and graft copolymers continue to attract both industrial and academic attention because of the retention of the unique features imparted by the siloxane component. PDMS oligomers of defined molecular weight and functionality were prepared from hexamethylcyclotrisiloxane using an anionic ring opening polymerization mechanism. Subsequently, block and graft copolymers of PMMA and PDMS were prepared using, respectively, a transformation synthesis, and the macromonomer technique. Both of these methods provide a means to prepare multicomponent materials by coupling different mechanisms; GTP and anionic ring opening. Though copolymers were isolated and characterized, as will be addressed, the efficiency of GTP for the formation of these PDMS containing copolymers appears to be hindered by an interesting mechanistic limitation.

CHAPTER II

LITERATURE REVIEW

INTRODUCTION

HISTORIC PERSPECTIVE. The roots of acrylic and methacrylic ester polymers stem back to the 1901 dissertation of Otto Rohm written at the University of Tübingen, Germany. Yet, it was not until World War II that these unknown materials were brought to the world's attention. During the war, acrylic materials were transformed into essential and standard elements of wartime commerce. Cast sheets of poly(methyl methacrylate) (PMMA), of which plexiglas was the leading example, formed the transparent portion of every aircraft in the allied arsenal. Indeed, this is a classic case of both international technology transfer and, unfortunately, war as accelerator of technological change [1,2]

Since 1942, acrylic and methacrylic ester polymers have become extremely versatile building blocks for the design of high quality products and hence have been woven into numerous areas of commerce. The practical application of these polymers in industry, whether it be in the area of fibers, coatings, plastic materials, or adhesives [7] has demonstrated the necessity of designing materials which have a balance of different properties [2]. The physical and chemical properties of polymeric systems are dependent upon molecular weight, stereochemistry and polymer structure. Although the molecular weight influences the physical and chemical properties of polymers, the properties of acrylic based polymers are also strongly influenced by the nature of the ester alkyl substituent and the microstructure. By judicious choice of the ester alkyl group and control of the tacticity for acrylic and methacrylic ester polymers, one can selectively influence the mechanical and thermal properties, thus tailoring a particular homopolymer, copolymer or blend to a selected application. This review of the literature will continue with a general description of the effects which the ester substituent and stereochemistry subsequently have on the properties of these polymers, prior to addressing the mechanisms of polymerization.

LITERATURE REVIEW

EFFECT OF THE ESTER ALKYL SUBSTITUENT. Poly(alkyl acrylate)s and poly(alkyl methacrylate)s are simply unsymmetrically substituted ethylenes. It is the substituents of the α -carbon of these α,β -unsaturated esters that give rise to the chemical structure and microstructure that so readily influences their thermal and mechanical properties. Acrylic ester polymers have a flexible backbone and are substituted by an ester alkyl group. In contrast, the methacrylic ester polymers are stiffened, relative to the alkyl acrylate polymers, by the presence of a methyl substituent which restricts the freedom of rotation of the polymer backbone. The difference in the chemical structure of the repeat unit for a given alkyl ester group affords variations not only in the physical properties of the two classes of polymers, but also in the environmental stability. The presence of an α -alkyl substituent increases the stability of the poly(alkyl methacrylate)s towards light and chemical degradation relative to their poly(alkyl acrylate) counterparts [3,4]. This structural difference is also evidenced by variation in the mechanism of thermal degradation. Poly(alkyl acrylate)s thermally degrade by random chain scission, whereas poly(alkyl methacrylate)s low in the homologues series, depolymerize when heated. A zero order decomposition is observed which results in the recovery of high percentages of monomer. Since the decomposition generates monomer in a clean manner, many are

exploring this as a potential recyclization process which would satisfy some environmental concerns [2,4]. Though this seems a viable process for the recovery of alkyl methacrylate monomers, it is only applicable to those monomers low in the homologous series. When higher homologues or branched alkyl substituents are present, there may be thermal degradation of the alkyl substituents prior to monomer recovery, such as in the thermal decomposition of poly(*t*-butyl methacrylate). The latter results in the evolution of isobutylene and the generation of a poly(anhydride) [5].

Understanding the influence of the pendent ester group on properties can give insight into probable uses. Thus, numerous studies have been conducted to examine the effect of the nature of the ester alkyl group, as well as polymer microstructure on various properties [6-9]. F.K. Harold et al. [6], for example, examined the thermodynamically induced shear degradation of dissolved poly(*n*-alkyl methacrylate)s near demixing conditions. This fundamental study not only explored the general validity of the concept of thermodynamically induced shear degradation with poly(*n*-alkyl methacrylate)s, but allowed an understanding of the effect of various ester substituents on the stability of the polymer chain in the presence of higher alcohol components to be developed. This relationship is important in determining probable oil additive applications such as

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viscosity index improvers.

The glass transition (T_g) is another property that is readily influenced by the nature of the pendent ester group. For these α,β -unsaturated esters, the T_g decreases as the length of the ester alkyl group increases in a linear fashion. The observed decrease in the T_g is due to variations in the packing density and thus, an increase in free volume. As the length of the ester substituent becomes sufficiently long ($>$ n-dodecyl) the flexibility of the main chain is reduced due to side chain crystallization and hence, the T_g is observed to increase within the series. In addition, increasing the bulkiness of the backbone relative to a linear alkyl group results in the T_g increasing within a given class of isomers [4,7,10].

EFFECT OF MICROSTRUCTURE. Since the acrylic and methacrylic ester polymers have psuedoasymmetric carbons, variations in physical and chemical properties arise from changes in microstructure. Subtle changes in the T_g , for example, are influenced by the chain configuration. For various triad compositions, the observed T_g of poly(methyl methacrylate), for example, will shift over a broad temperature range. This range has upper and lower limits bounded on the high extreme by the T_g of polymers having a high syndiotactic microstructure and that of the low end by polymers of high isotactic chain configuration [11-13].

LITERATURE REVIEW

In 1958, researchers at Rohm and Haas reported the preparation of semi-crystalline polymers of poly(methyl methacrylate) [14]. Since that time, many have explored the ability to prepare poly(alkyl methacrylate)s with unusually uniform microstructure by a variety of methods as described in references 10, 15 and 16, and these will be addressed in further detail during the discussion of the various mechanisms of polymerization. It should be noted, that the ability to prepare tactic polymers is an advantage when one considers the ability to modify chemical and mechanical properties. For instance, blending materials of high tactic nature with conventional amorphous polymers has been shown to affect the mechanical properties. This phenomenon has been elegantly demonstrated by P.E.M. Allen et al. [12,17] in studies to examine molecular entanglements as one of the structural factors governing the fracture process. The fracture toughness of commercial atactic PMMA was significantly enhanced by blending it with isotactic PMMA. It was proposed that the entanglement density was increased by pseudocrosslinks which were due to the formation of polymer complexes between these two polymers. Crystallization of stereocomplexes at the crack tip inhibited chain disentanglements and reinforced the entanglement network to promote craze formation. The formation of stereocomplexes resulted in enhanced fracture toughness and this relationship suggests that the

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entanglement density plays a crucial role in the mechanism of cracking and crazing.

Other investigators have studied the solution characteristics of PMMA stereocomplexes [16-19]. These experiments elucidate the optimum ratio as well as the nature of the stereocomplex particles. The experimental methods employed have been classified into three categories based on the information they supply. Viscometry, light scattering and osmometry are techniques which supply information about the average molecular parameters and hence, the optimum ratio of isotactic to syndiotactic PMMA can be determined. Spectroscopic methods, such as NMR and IR, are sensitive to the complication of monomeric residues. The amount of associated polymer can be determined by separation methods like gel permeation chromatography [18-20].

SUMMARY. The trend of research in exploring the fundamental questions of the effects of stereochemistry and monomer structure on the physical and chemical properties stems from products emerging from industry into the market place. Whether these are new grades of well established products or products from novel materials, a tighter control of profile properties has been demanded than in the past. That is the linearity or branching, functionality, microstructure and molecular weight distribution of the

polymer chain are specified [21]. The result of preparing defined materials ultimately stems from the mechanism of polymerization employed and the reaction conditions (i.e. solvent and temperature) implemented during the polymerization process. α,β -Unsaturated esters are an interesting class of monomers which can be polymerized by a variety of chain polymerization mechanisms. This will be the primary focus of the succeeding portion of the literature review. Emphasis will be placed on a detailed discussion of group transfer polymerization (GTP) with a brief discussion of the characteristics of free radical and anionic polymerization mechanisms.

POLYMERIZATION MECHANISMS

INTRODUCTION. The reactivity of acrylates and methacrylates with electrophilic, free radical and nucleophilic reagents is well documented in the organic literature [22]. The transformation of acrylic and methacrylic esters into long chain macromolecules proceeds through chain polymerization involving the addition of monomer to an activated or an initiated form of the monomer. This chain polymerization process involves three basic steps; initiation, propagation and termination, and the details of these three events are highly mechanism

LITERATURE REVIEW

dependent. The reactive intermediates may be either radicals, anions or coordinated species, depending on the mode of polymerization.

FREE RADICAL POLYMERIZATION. The free radical polymerization of vinyl monomers is a classic example of chain polymerization and its diversity is especially apparent when discussing the polymerization of alkyl acrylates and alkyl methacrylates. These monomers are conveniently polymerized to high molecular weight and conversion by a number of processes. Table 1 briefly outlines the advantages and disadvantages of each of these processes [23]. A more in depth discussion of the details and mechanistic considerations for each of these processes can be found in references 2, 24 and 25.

The general mechanism of polymerization for α,β -unsaturated esters via a free radical process is illustrated in Scheme 1 for the polymerization of MMA. The initiator decomposition step involves the generation of radical species which will act as the initiator of polymerization. This may be accomplished by the thermal decomposition of an initiator such as an azo or peroxide compound [26] or the generation of radicals from aromatic ketone compounds through hydrogen abstraction and photofragmentation [27]. Other methods of generating radicals include the use of

TABLE 1: COMPARISON OF VARIOUS POLYMERIZATION PROCESSES

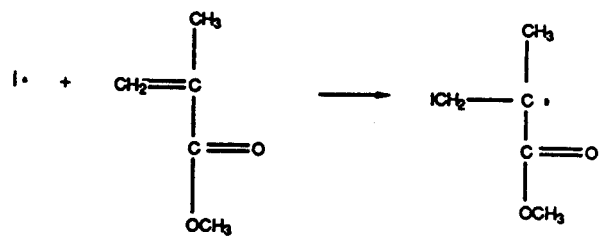
PROCESS	ADVANTAGES	DISADVANTAGES
Bulk(Batch)	Low impurity level.	Thermal control difficult.
Bulk(Continuous)	Improved thermal control.	Product isolation difficult; requires devolatilization.
Solution	Improved thermal control.	Solvent removal difficult. Solvent recovery costly. Chain transfer may limit molecular weight.
Suspension	Low viscosity. Simple polymer isolation. Thermal control. Particle size may be directly usable.	Highly sensitive to agitation rate. Difficult to control particle size. Contamination possible by suspending agent. Washing, drying and compaction may be necessary
Emulsion	Low viscosity. Thermal control. Latex may be directly usable. High conversions possible. High MW, at high rates. Small particle size obtainable. Operable with soft tacky polymers.	Removal of emulsifier, surfactants, and coagulants. Degradation of certain polymer properties due to a high level of residual impurities. High cost. Washing, drying, and compacting may be necessary.

Ref.23. McGrath, J.E J. Chem Ed. 1981, 844.

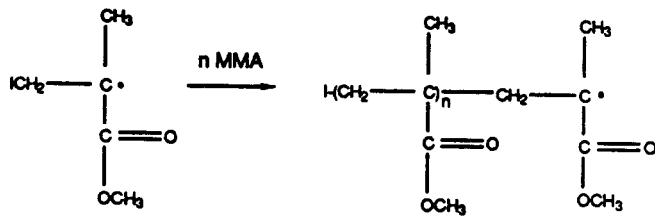
Initiator
Decomposition



Initiation



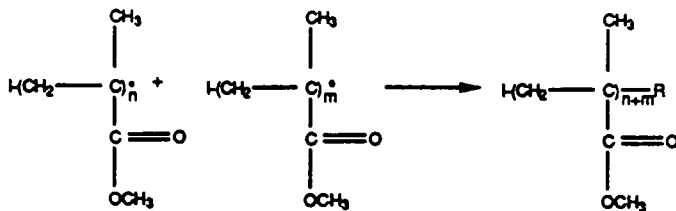
Propagation



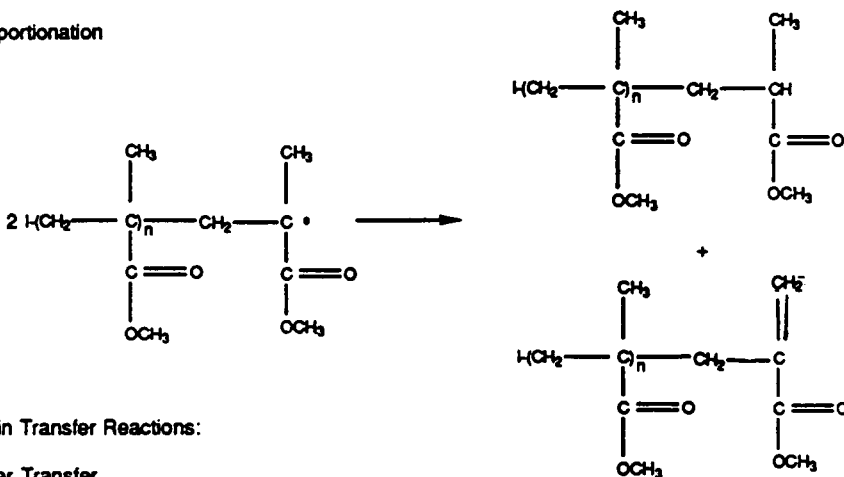
Scheme 1. Free Radical Polymerization of MMA

Termination :

1) Combination

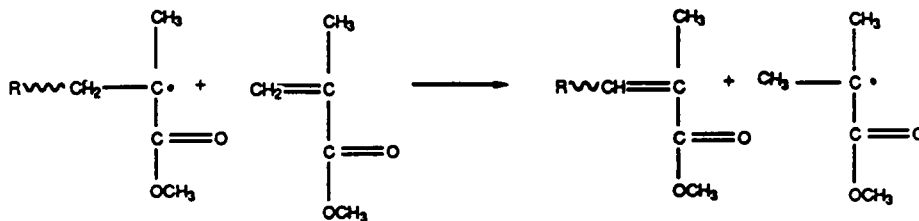


2) Disproportionation

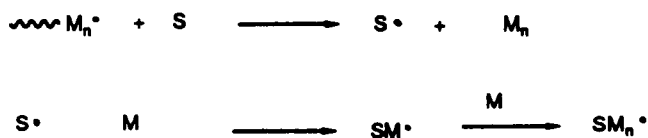


Selected Chain Transfer Reactions:

1) Monomer Transfer



2) "Solvent" Transfer



Scheme 1 (continued). Free Radical Polymerization of MMA

radiation or redox initiation via electron transfer [25]. Many details of the chain initiation process and characterization of the various initiating species have been elucidated through studies using ^{14}C labeling, electron spin resonance (ESR), deuterated monomer techniques, as well as flash photolysis in combination with various spectroscopic methods [26-29]. Giving particular attention to the initiation step, the selection of the initiating species is dependent on a number of factors. These include the solubility of the initiating species in the polymerization solvent, rate of initiator decomposition, end groups desired, and intended use of the polymer.

The free radical polymerization proceeds with chain propagation which entails the head-to-tail growth of the polymeric free radical by attack on the double bond of the monomer. The head-to-tail configuration is favored due to resonance as well as steric considerations. The resulting stereochemistry of the polymer develops with chain propagation and is a very important parameter as we have already discussed. Table 2 shows the microstructure of poly(methacrylic ester)s prepared with a variety of free radical initiators [11]. In general, these polymers have predominantly a syndiotactic nature which decreases with increasing bulkiness of monomers having secondary and tertiary ester groups, yet increases with decreasing

TABLE 2: MICROSTRUCTURE OF FREE RADICALLY
PREPARED POLY(ALKYL METHACRYLATE)S

Alkyl Methacrylate	Initiator	Temperature (°C)	Triad Content, %		
			I	H	S
methyl	BPO	60	4	34	62
n-butyl	AIBN	70	8	27	65
t-butyl	BPO	70	8	40	52
trityl	AIBN	60	64	22	14

I = Isotactic (mm)

H = Heterotactic (mr)

S = Syndiotactic (rr)

BPO = Benzoyl peroxide

AIBN = 2,2'-Azobisisobutyronitrile

Ref.11. Yuki, H.; Hatada, K. In Advances in Polymer Science;
Cantow, H.J., Ed.; Spinger-Verlag: New York, 1979;
Vol.31, pp. 1-45.

temperature. Aromatic poly(methacrylate)s have higher isotacticity than the corresponding aliphatic or cycloaliphatic polymers. This is extremely evident with trityl methacrylate. The bulky trityl group of the monomer and propagating chain may force the addition mode of monomer to be more favorable to meso dyad configuration resulting in high isotactic triads [30]. Recent attempts to obtain tactic polymers via a free radical mechanism have involved template polymerizations which take advantage of the ability of isotactic and syndiotactic PMMA to form stereocomplexes [31,32].

The choice of polymerization solvent is not only important when selecting the initiating species, but the course and mechanism of reaction are readily influenced by the solvent [33,34]. The choice of solvent for the polymerization is particularly important when one considers the effect of chain transfer on polymerization kinetics, molecular weight and end groups. Chain transfer, in general, involves a growing chain interacting with a small molecule in such a way that a portion of the small molecule can terminate the active radical and produce a new radical. There are many chain transfer steps, such as transfer to monomer, to solvent, to initiator, to polymer, or even to a modifier. The amount of chain transfer is dependent on the reactivity of the growing radical with the small molecules present in the system. Chain transfer agents are available

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which enable molecular weight to be controlled other than by initiator concentration and type, solvent concentration and type, monomer, and temperature [2,25].

Polymer molecular weight, as well as a decrease in the rate of monomer reaction and kinetic chain length, is affected by the presence of oxygen. Acrylate and methacrylate polymerizations are markedly inhibited by oxygen due to the copolymerization of the growing radical with oxygen producing a terminal peroxy radical which slowly reacts with monomer yet, has a relatively rapid termination step. In the absence of oxygen, chain termination can occur by either combination or disproportionation, depending on the conditions of the process. Termination by combination results in the interaction of two growing macroradicals to form an inactive species. If no chain transfer has occurred then the resulting polymer chain will possess two initiator fragments which is desirable when considering post reactions such as chain extension for the preparation of novel segmented copolymers. Alternatively, termination can occur via disproportionation which again involves two macroradicals terminating each other. In this case however, one chain has a saturated group due to hydrogen abstraction while the other has an unsaturated end group. Both processes of termination in general are quite rapid and involve a rather low energy of activation which eventually

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allows one to use steady state assumptions when solving the equation for the polymerization rate [23,25].

Though the polymerization rate expression is simplified, the influence of the termination mechanism cannot be forgotten when considering the thermal and oxidative stability of these polymers. Kashiwagi et al. [35], have examined in detail the thermal and oxidative degradation mechanisms of PMMA in both air and nitrogen atmospheres. They have examined many factors, including the effect of chain transfer agents, type of initiator, effect of molecular weight and the low temperature degradation in the presence of gas phase oxygen. Understanding thermal stability gives insight into the possible reactions that may occur during the final processing of these polymers. The degradation of free radically prepared PMMA in nitrogen may be initiated by one of three reactions. The least stable reaction is chain scission at head-to-head linkages which is observed to occur around 165 °C for a heating rate of 2 C/min. The second reaction, at about 270 °C, is chain end initiation from vinylidene chain ends. The most stable is random scission within polymer chains which initiates degradation around 360 °C.

Smith and McGrath [36] have demonstrated an alternative way, other than anionic polymerization, of achieving enhanced thermal stability for PMMA prepared by a free radical mechanism. Utilizing the macromonomer technique,

methacrylate functionalized poly(dimethylsiloxane) (PDMS) oligomers were copolymerized with methyl methacrylate under free radical polymerization conditions. The initial results indicate enhanced thermal stability for the graft copolymers, which may partially be explained by the antioxidant character of PDMS.

The reactivities of acrylic monomers and other vinyl monomers are similar under the conditions of free radical polymerization. This, in conjunction with the ability of these monomers to stabilize the propagating radical over two or more atoms, allows for the preparation of a variety of copolymers. Though homopolymers and fairly random, short sequenced homogeneous copolymers can be synthesized via free radical techniques, the resulting molecular weight distributions are broad and molecular weight control, in some cases, is difficult to maintain. Under the proper conditions, a controlled mechanism of polymerization will enable well defined materials to be prepared. The literature review will continue with a brief discussion of the characteristics of anionic polymerization before addressing in detail the mechanism of GTP.

ANIONIC POLYMERIZATION. It is well recognized that the precise control of polymer parameters (molecular weight, molecular weight distribution, stereochemistry, functional termination, copolymer composition and architecture) is the

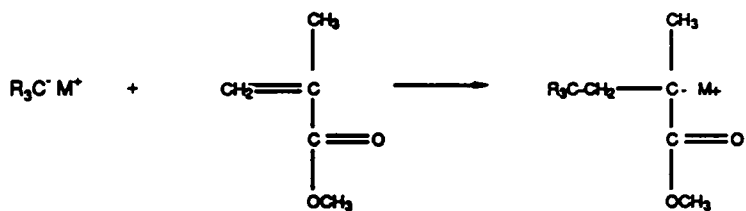
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key to optimizing and understanding physical properties. Ionic routes, by their nature, permit the tailoring of polymer structure. Of particular interest is the anionic polymerization mechanism. The anionic polymerization of styrenes and dienes has received a significant amount of attention due to the commercial importance of these processes [37,38]. In comparison, the anionic polymerization of acrylic and methacrylic ester polymers is of minor commercial significance resulting from the presence of protic impurities in commercial grades of monomers and the high carbanionic reactivity promoting side reactions with polar substituents.

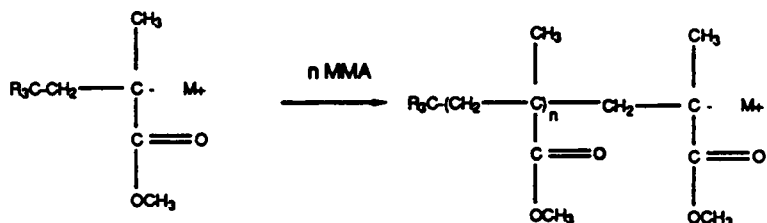
Control of reaction conditions (monomer purity, solvent and temperature) permit the anionic polymerization of α,β -unsaturated esters to form stereoregular, block or telechelic polymers having controlled molecular weights and narrow molecular weight distributions. A number of reviews cover these and other aspects of the anionic polymerization of alkyl acrylates and methacrylates [15,25,39-41].

In general, initiation is considered to take place via a Michael reaction (Scheme 2). Rapid initiation kinetics, a characteristic of many "living" anionic polymerizations, affords polymers of narrow molecular weight distributions and controlled molecular weights, since in principle all chains begin to grow at the same time. The ability of a reagent to generate the propagating, delocalized anion

Initiation



Propagation



Scheme 2. General Initiation and Propagation Steps for the Anionic Polymerization of MMA

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depends on the reactivity of the monomer toward nucleophilic attack. Due to the strongly electron-withdrawing substituents which also stabilize the propagating carbanion, alkyl methacrylates can even be polymerized to some degree in dipolar aprotic solvents by weaker nucleophiles such as alkoxide ions [42]. A large number of anionic initiators and initiating systems have been utilized in the polymerization of PMMA. Yuki et al., [11] and Erusalimiskii [15] summarize the studies conducted, examining the effect of various initiators and polymerization conditions on the structure of PMMA. Alkyl lithium initiators are among the most useful anionic initiators, and are employed commercially for the polymerization of isoprene and butadiene [37]. Though these initiators are of both industrial and academic importance, deleterious side reactions can occur with polar monomers resulting in destruction of the initiator. Unhindered alkyl lithium initiators react with the pendent ester group of the monomer forming vinyl ketone monomer resulting in the loss of molecular weight control [43,44].

Alternatively, other investigators have demonstrated that the adduct of sec-butyllithium and 1,1 diphenylethylene form an initiator which efficiently initiates polymerization of vinyl monomers [45,46]. The bulkiness and the lower basicity of the diphenylhexyllithium (DPHL) carbanion

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permits initiation of methacrylic esters with no detectable carbonyl attack at -78°C in tetrahydrofuran [39,47].

Once formed, the delocalized enolate is capable of attacking more monomer forming a propagating carbanion which may remain active for extended periods of time. This "living" property allows for the synthesis of block copolymers of controlled composition via sequential monomer addition. The "living" character is maintained in the absence of specific reagents, such as oxygen and active hydrogen species (i.e. water and alcohols). Deleterious protic impurities can be removed from the monomer prior to homo- or copolymerization. Heterogeneous drying agents, for instance calcium hydride, react with impurities like water but, they do not react with alcohols. Alcohols are traditionally present in commercial grades of acrylic and methacrylic esters due to the method of commercial synthesis of these materials [2,39]. Allen et al. [48-50], have investigated a novel purification methodology involving trialkylaluminum and dialkylaluminum hydride reagents as homogeneous drying agents. The alkyl aluminum compounds react readily with protic impurities and form a stable complex with the methacrylate monomers. Hence, the monomer can be titrated and distilled from the yellow-green complex yielding ultra-pure monomer.

The head to tail addition of monomer to the polymeric carbanion gives rise to the resulting microstructure. Table

TABLE 3: MICROSTRUCTURE OF POLY(METHYL METHACRYLATE)
PREPARED WITH A VARIETY OF ANIONIC INITIATORS

SYSTEM	TRIAD CONTENT, %			REF.
	I	H	S	
s-Butyllithium toluene, -78 °C	68	19	13	39
DPHL, toluene, -78 °C	82	15	3	47
DPHL, THF, -78 °C	1	21	78	47
t-Butylmagnesium bromide, toluene/THF 50 °C	84	6	10	15
t-Butylmagnesium bromide, toluene/THF 50 °C	84	6	10	15
EtMgO-isoBu toluene, -78 °C	91	4	5	11
Fluorenyl cesium THF, -78 °C	5	46	49	16
Octylpotassium THF, -78 °C	11	53	36	16
Na / THF	4	36	58	41
Cs /THF	5	53	42	41

I = Isotactic (mm)

H = Heterotactic (mr)

S = Syndiotactic

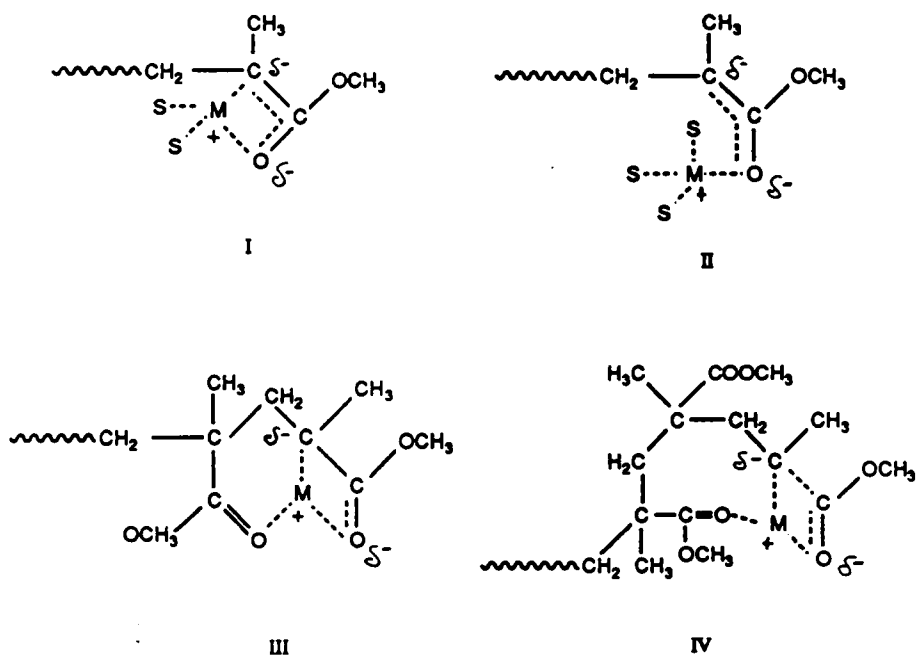
DPHL = 1,1 Diphenylhexyllithium

THF = Tetrahydrofuran

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3 illustrates the microstructure of poly(methyl methacrylate)s prepared under a variety of anionic reaction conditions. The observed microstructure is readily influenced and controlled by appropriate choice of initiator, solvents and temperature [16,39,47,51,52]. For example, polar solvents promote ion pair dissociation and polymers having high syndiotactic microstructure are prepared at low temperatures. The syndiotactic placement is dominated by interactions between the propagating chain end and the incoming monomer. Isotactic polymers, on the other hand, can be prepared in nonpolar solvents. Tight ion pairs under these conditions enhance the participation of counterions in directing monomer placement to predominantly one configuration. Numerous investigations have been carried out to determine the nature of the active centers in anionic polymerization of polar monomers [40,53-56]. Despite these efforts, there is no generally accepted theory explaining the causes of stereoregulation in acrylic and methacrylic ester anionic polymerizations. Based on kinetic measurements using various counterions and solvents of varying solvating power, one theory proposed suggests that part or all of the active species exist in a special form of a contact ion pair. Structures I and II (Scheme 3) have been proposed to represent the structure of the ion pair. The "true" structure may lie between these two depending upon the solvent, counterion and temperature. The

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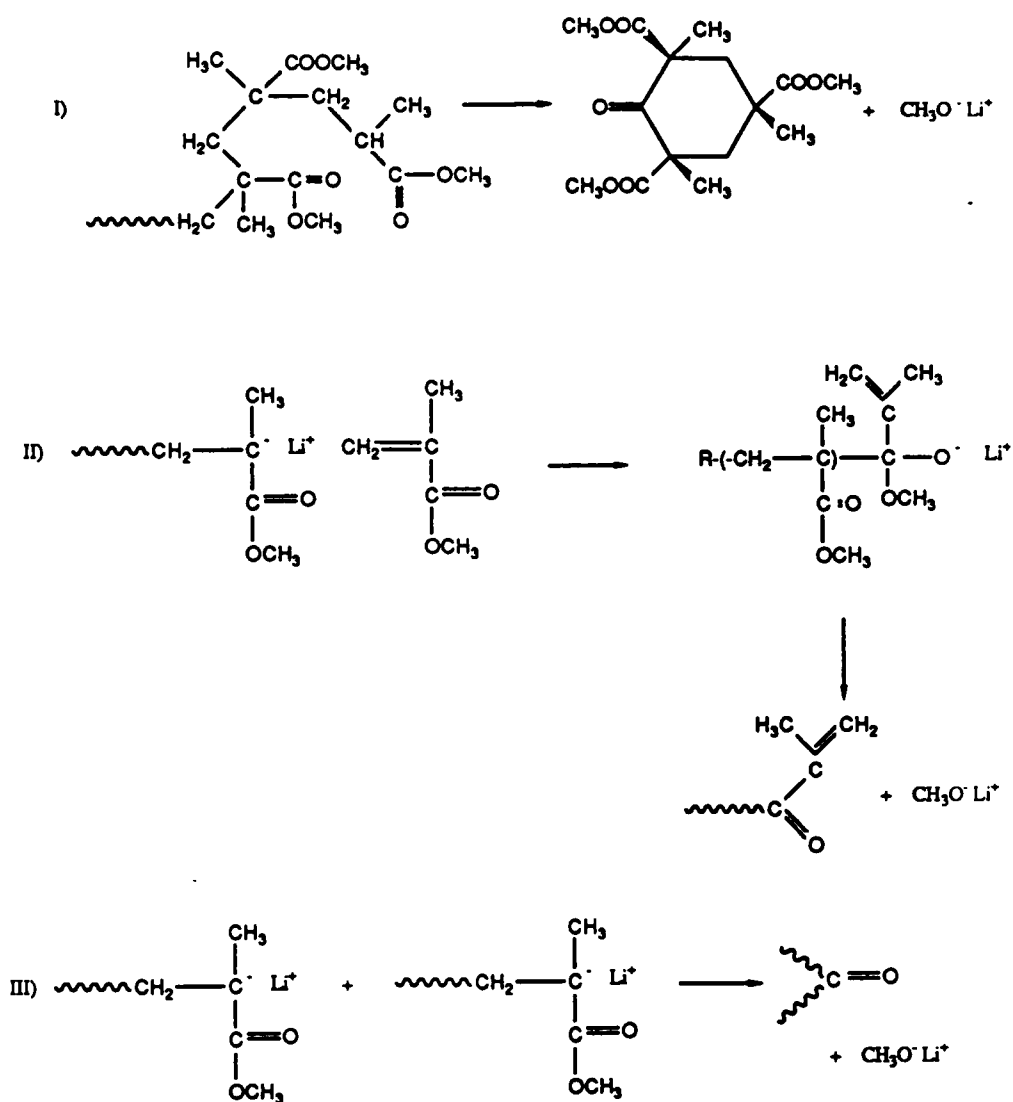
40. Müller, A.H.E. In Anionic Polymerization: Kinetics, Mechanism, and Synthesis; McGrath, J.E., Ed.; ACS Symposium Series 166; American Chemical Society: Washington DC, 1981; 441-461.

Scheme 3. Proposed Ion Pair Structures

propagating carbanion may also exist in part as structure III or IV. This is especially possible in solvents, like THF, which are less solvating than DMF or acetonitrile. These structures, III and IV, have been proposed by Fowells et al., whose rather speculative model assumes the counterion to be solvated intermolecularly by the penultimate or antepenultimate ester group of the polymer chain end [40].

A favorable amount of attention is now being directed to the preparation of heterotactic poly(alkyl methacrylate)s. The ability to obtain polymers with this microstructure would require a higher order of stereoregulation than for isotactic or syndiotactic polymers and may involve a different form of the contact ion pair. Initial investigations indicate that not only the size of the pendent ester group is important, but the nature of the counterion and polymerization medium play a crucial role [16].

The stability of the propagating enolate is strongly influenced by the polymerization temperature. Generally, the stability of the carbanion is reduced as the temperature is increased. Loss of stability promotes side reactions associated with the ester carbonyl. Assuming the initiator has not attacked the monomer first to form a vinyl ketone as addressed previously, three main termination reactions can result. The side reactions depicted in Scheme 4 are [25]:



25. Odian, G. Principles of Polymerization, 2nd ed.; John-Wiley and Sons: New York, 1981.

Scheme 4. Possible Termination Mechanisms in the Anionic Polymerization of MMA

- I. An intermolecular cyclization of the trimer producing a six membered ring
- II. Reaction of the anionic propagating center with the ester group of the monomer
- III. Reaction of the propagating enolate with the ester group of the polymer chain

The marked instability of the propagating chain end, requiring very low temperatures, is a major deficiency and renders the commercial polymerization of alkyl methacrylates via anionic techniques unattractive and uneconomical.

Side reactions associated with the ester carbonyl are even more evident in the polymerization of alkyl acrylates via anionic methods. These side reactions, and the presence of the acidic α -hydrogens prevents the polymerization of these monomers to high conversion under controlled conditions [57-59]. Taking advantage of the concept of ion pairs and the ability of ligands to alter the kinetics and mechanism of anionic polymerizations, Teyssie et al., [60-62] have investigated the use of inorganic salts, such as lithium chloride, to polymerize sterically hindered alkyl acrylates and alkyl methacrylates in a "living" manner. The salts are able to complex to the propagating chain end altering the reactivity of the anion and reducing transfer and termination reactions. Also, lithium chloride is a ligand that is able to alter the ion pair structure in such a way that apparently counterbalances the unfavorable

termination reactions that occur at increased temperatures, thus allowing an essentially living polymerization [60,63].

In the absence of termination reactions, anionic techniques provide a suitable route for the preparation of polymers having functional end groups, functional groups in the backbone, as well as block copolymers via sequential monomer addition. Functional end groups can be introduced through the use of masked initiators or through capping reactions [64]. Although polymers with functional reactive end groups can serve as building blocks for copolymers of predetermined structure, sequential addition of monomers to a living polymerization is one of the most useful method of preparing block copolymers [65]. These methods for the preparation of multicomponent systems will be described in more detail later in this review of the literature.

In view of these important features of anionic polymerization noted above, and the requirements necessary for acrylic and methacrylic ester monomers, a tremendous amount of interest has been generated in the fundamentally new polymerization technique, Group Transfer Polymerization. This latter polymerization route, established by Webster et al. [66-67] at duPont, enables the polymerization of monomers, such as methyl methacrylate, in a "living" manner with high chain end stability over a broad temperature range. The degree of control over molecular weight and molecular weight distribution rivals that afforded through

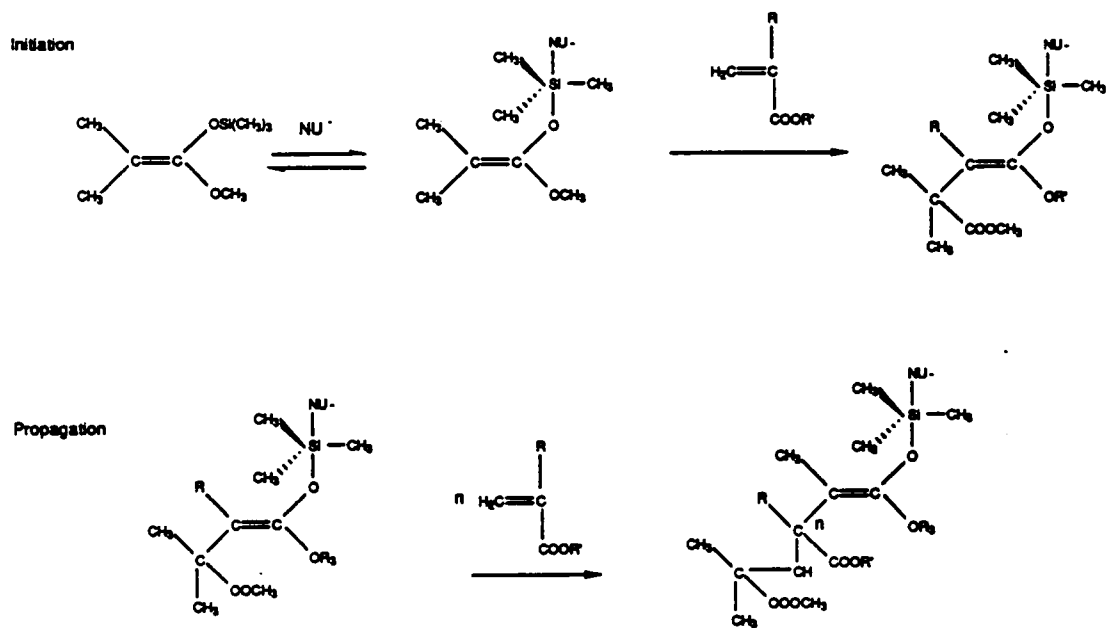
living anionic polymerization methods for the preparation of poly(alkyl methacrylate)s. Emphasis of the literature review will now be directed to a detailed discussion of GTP. The essential features of GTP will be reviewed as well as the mechanistic and kinetic behavior of this polymerization process.

GROUP TRANSFER POLYMERIZATION

INTRODUCTION. The term, group transfer polymerization, was coined from the observation that in general, this process proceeded by the repeated addition of a trialkylsilyl group from the initiator, a ketene silyl acetal, or the growing chain end to the incoming monomer (Scheme 5) [66]. This transfer occurred in conjunction with the concerted addition of that monomer to the growing chain, in the presence of a catalyst. Prior to addressing the mechanism and kinetics of polymerization, a brief discussion of the characteristics of the initiators, catalysts, monomers and solvent systems will be presented.

INITIATORS. Ketene acetals, in general, have been reported in the literature since 1907 [69]. The first recognized ketene trialkylsilyl acetal was prepared by Petrov in 1959 by the reaction of triethylsilane and methyl methacrylate [69]. Ketene silyl acetals since then have

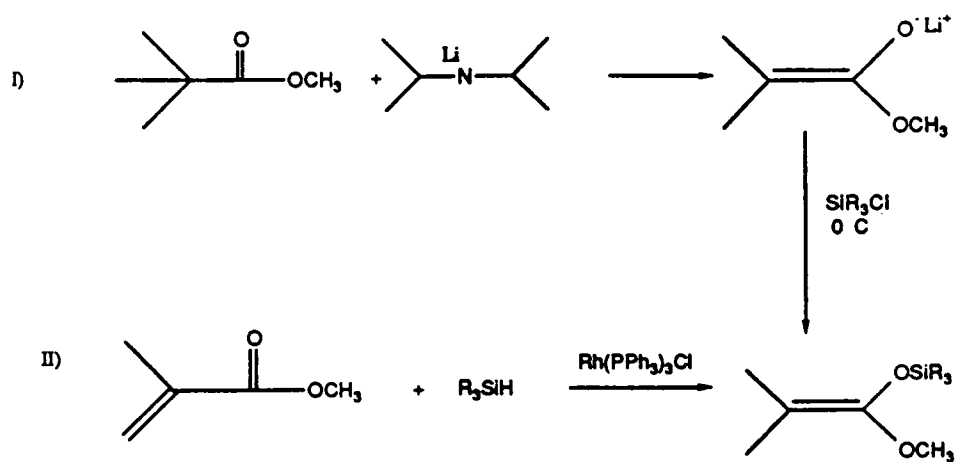
LITERATURE REVIEW



66. Webster, O.W.; Hertler, W.R.; Sogah, D.Y.;
Farnham, W.B.; RajanBabu, T.V. J. Am. Chem. Soc. 1983,
105(17), 5706-5709.

Scheme 5. GTP Initiation and Propagation of Alkyl Methacrylates

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Scheme 6. Preparation of Ketene Silyl Acetals

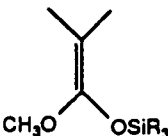
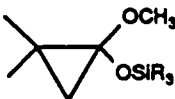
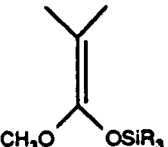
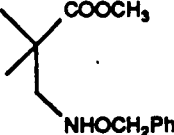
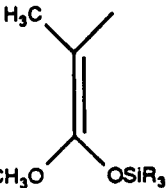
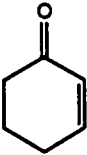
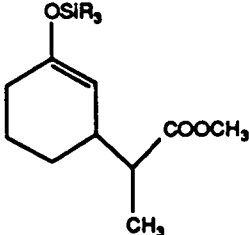
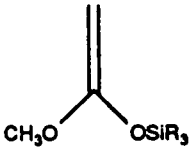
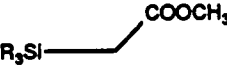
been prepared by various methods which yield varying amounts of C- and O- silylated products. Scheme 6 illustrates the preparation of silyl ketene acetal by two different synthetic pathways. The first route (I) involves the preparation of silyl ketene acetals from α -anions of acetates and trimethylchlorosilane (TMCS). The α -anion is formed by the addition of lithium diisopropylamide (LDA) to an ester, followed by the addition of TMCS [69,70]. An alternative approach is depicted in pathway 2 of Scheme 6 [71,72]. In this synthetic pathway, tris(triphenyl)-phosphinechlororhodium (Wilkinson catalyst) quite effectively catalyzes the hydrosilylation of α,β -unsaturated esters to afford 1,2-adducts or 1,4 adducts selectively in high yields, depending upon the esters and hydrosilanes used. The hydrosilylation of methyl methacrylate in the presence of Wilkinson's catalyst affords 93% of the 1,4 addition product, the ketene silyl acetal.

Ketene silyl acetals are utilized in organic synthesis to prepare a wide variety of materials. Table 4 depicts a sample of the facile synthesis that can be accomplished using ketene silyl acetals [73-76]. The silylation of materials using ketene silyl acetals requires a catalyst which may vary from anions to Lewis acids, depending on the mechanism involved.

Taking advantage of the synthetic versatility of ketene silyl acetals, workers at duPont have effectively applied

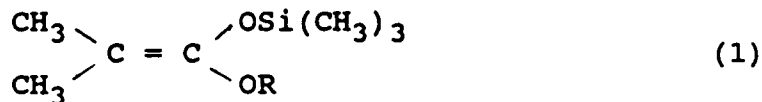
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Table 4. Facile Synthesis using Ketene Silyl Acetals

KETENE SILYL ACETAL	REAGENTS	PRODUCT	REF.
	<chem>CH3I, Et2N</chem>		73
	<chem>CH2=NOCH2Ph, CH2Cl2, RT, 5 Hrs.</chem>		74
	 <chem>55 C, 4 Hrs.</chem>		75
	<chem>Hgl2, Δ</chem>		76

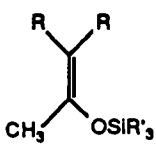
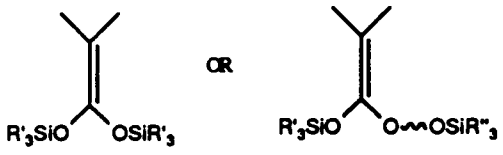
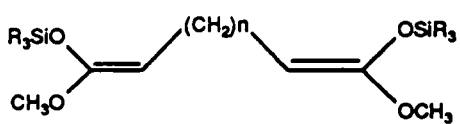
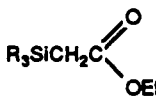
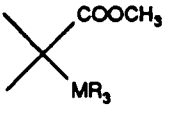
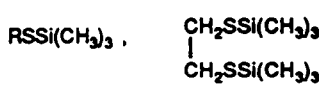
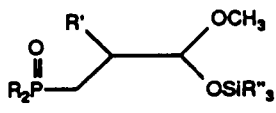
the reactivity of these compounds to the preparation of acrylic and methacrylic ester polymers. A diverse number of initiators have been effectively employed in group transfer polymerization. A number of these are listed in Table 5. A more comprehensive array is documented in the duPont patents [67]. Likewise, Sogah et al. [77], have recently reviewed the preparation of the various initiators and the subsequent initiation of the polymerization of α, β -unsaturated esters with these.

The ketene silyl acetal structure is regenerated each time the trialkylsilyl group is transferred to an incoming methacrylate monomer, thus the most common initiators have a structure of 1-alkoxy-1'-(trimethylsiloxy)-2-methyl-1-alkene (1).



As documented by Webster [68,79], these are the most effective initiators and alteration of the substituents may influence the reactivity or the nature of the polymer end groups. For instance, when steric requirements become quite large for the alkyl substituents on the trialkylsilyl fragment, a reduction in the polymerization rate is generally observed [77]. Also, loss of molecular weight control has resulted upon exchange of the β -methyl group for

Table 5. Select List of GTP Initiators

GTP INITIATORS	REF.
	66,71
	64,77,78
	83
	70,66
	<p>M = Ge, Sn</p> <p>77,89</p>
R_3SiCN	66,85
	86
	82

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a hydrogen atom when nucleophilic catalysts have been employed. This may be explained by the ability of nucleophilic catalysts (HF_2^-) to catalyze the isomerization of the ketene silyl acetal to an α -silyl ester. The equilibrium is strongly shifted to the formation of C-silylated material resulting in an α -silyl ester, when at least one of the β substituents of the ketene silyl acetal is a hydrogen atom. These C-silylated compounds are inactive forms of the initiator resulting in a loss of molecular weight control as confirmed by employing β -silyl ethers as initiators [77].

Masked initiators have been successfully employed in GTP for the preparation of chelic, and telechelic polymers having a variety of functional reactive end groups [64,77,78]. These protected initiators give rise to a variety of functional groups; hydroxyl [64,77], carboxylic [64,77], acyl [80] and styrenic groups [81]. Polymers containing terminal phosphonic acid groups were uniquely prepared by Hertler et al. [77,82], from phosphorous containing ketene silyl acetals. In general these initiators required unusually high levels of catalyst. This was attributed to the coordination of the catalyst to the phosphonate group rendering it inactive during polymerization. However the use of phosphonamide based initiators, which are less likely to coordinate to nucleophiles, required no additional catalyst. The facile

design of initiators leads to a variety of architectures including blocks, grafts or combs, ladders and stars [77,83,84].

A number of silyl derivatives initiate the GTP mechanism. These silyl derivatives include trimethylsilyl cyanide [77,85], alkylthiosilanes and arylthiosilanes [86]. These derivatives are capable of reacting with α,β -unsaturated esters by a catalyzed Michael addition to form a ketene silyl acetal in situ, followed by polymerization. Banderman et al. [85,87,88], have investigated the characteristics and kinetics of the GTP of using trimethylsilylcyanide as the initiator. The effect of these silyl derivatives on the mechanism and kinetic aspects will be addressed later in this review.

Group transfer polymerization is not limited to the transfer of a trialkylsilyl group. Analogues of these silicon containing initiators have been prepared containing tin and germanium [77,89,90]. Studies indicate poor molecular weight control and a broadening of the molecular weight distribution of PMMA prepared with these initiators. This has been attributed to the change of the steric environment at the living chain end for these organotin and organogermanium initiators relative to their silicon containing analogues [77].

Regardless of the initiator structure, the resulting propagating chain end has the structure of a ketene silyl


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acetal. Propagation, as well as initiation, occurs via the transfer of the trialkylsilyl group to the incoming monomer unit. This transfer occurs in the presence of either nucleophilic or electrophilic catalysts. The various types of catalysts which have been employed in the GTP mechanism will now be addressed.

CATALYSTS. The GTP process is catalyzed by a variety of reagents which fall into two general classes, nucleophiles and electrophiles (Table 6). The role of the catalyst in the polymerization mechanism appears to change depending on its nature. Electrophilic catalysts, such as Lewis acids have been proposed to activate the monomer toward nucleophilic attack by the ketene silyl acetal chain end. Whereas, nucleophilic catalysts find their role in coordinating to the silicon atom of the initiator or propagating chain end producing a pentacoordinate intermediate that is more reactive toward coordination with an incoming monomer [93]. Although difluoromethylsilicate, cyanide, acetate, and benzoate have been successfully applied as GTP catalysts, the bifluorides have been most extensively utilized.

Fluoride and bifluoride catalysts are recognized desilylating agents [94]. Due to their strong affinity for silicon, these reagents have also been found to be very efficient in promoting a variety of organic reactions. For

TABLE 6: CATALYSTS FOR GTP

Catalyst	Structure	Ref.
Tris(dimethylamino)-sulfonium bifluoride (TASHF ₂)	$[(\text{CH}_3)_2\text{N}]_3\text{S}^+ \text{HF}_2^-$	66,77
Tris(dimethylamino)sulfonium difluorotrimethyl silicate (TASF ₂ SiMe ₃)	$[(\text{CH}_3)_2\text{N}]_3\text{S}^+ \text{Si}(\text{CH}_3)_3\text{F}_2^-$	77,85
Tris(piperidino)sulfonium bifluoride (TPSHF ₂)	$[\text{Piperidine}]_3\text{S}^+ \text{HF}_2^-$	91
Tetra(alkyl) ammonium - cyanide	$(\text{alkyl})_4\text{N}^+ \text{CN}^-$	87,91
Tetra(alkyl)-ammonium acetate	$(\text{R})_4\text{N}^+ \text{}^- \text{OOCCH}_3$	92
Tetra(alkyl) ammonium benzoate	$(\text{R})_4\text{N}^+ \text{}^- \text{OOC}$ 	92
Zinc Halides	$\text{ZnCl}_2, \text{ZnBr}_2, \text{ZnI}_2$	77,93
Di(alkyl) aluminum-chloride	R_2AlCl	77,93
Di(alkyl) aluminum oxide	$(\text{R}_2\text{Al})_2\text{O}$	77,93

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example, cesium fluoride in the presence of trialkoxysilanes ($\text{Si}(\text{OR})_3\text{H}$) promotes Michael additions of monoketones and arylacetoneitriles on different kinds of Michael acceptors such as α,β -unsaturated ketones, esters, nitriles and amides [95]. In the presence of a catalytic amount of tetrabutylammonium fluoride (TBAF), Kita et al., [96] utilized the reactivity of ketene methyl trimethylsilyl acetals to prepare a variety of cyclic oxygen-oxygen, oxygen-sulfur, and sulfur-sulfur acetals from enolizable carbonyl compounds.

These fluoride and bifluoride compounds have also been successfully employed as catalysts in GTP of alkyl methacrylates [74,75,77]. The most frequently employed and studied catalyst is tris(dimethylamino) sulfonium bifluoride (TASHF_2) [97]. Hydrolysis of tris(dimethylamino)sulfonium difluorotrimethylsiliconate yields TASHF_2 , a crystalline solid, which is soluble in a variety of organic solvents. It is the counterion of these anions that determines the solubility of the salt. Catalysts, such as TASHF_2 and potassium bifluoride (KHF_2) are soluble in solvents having high solubility parameters (acetonitrile, and dimethylformamide). When solvents of lesser polarity are employed with these catalysts, a cosolvent is typically utilized. Despite the low solubility of TASHF_2 in THF, the polymerization of MMA with a heterogeneous mixture of solid

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TASHF₂ in THF has been demonstrated to yield controlled molecular weight and narrow polydispersity [77].

Alternative nucleophilic catalysts include cyanide, and oxy-anions. Typical cyanide catalysts include tris(dimethylamino)sulfonium cyanide [77] and tetraethylammonium cyanide [77,87,88]. Polymerizations carried out in THF again resulted in good control over the molecular weight and molecular weight distribution. However, counterions, like the tetraethylammonium have limited solubility in solvents of low polarity, hence; a co-solvent is typically charged to obtain a homogeneous system [77].

The breadth of catalysts for GTP was further expanded by duPont scientists in 1987, when Dicker et al. [92] reported on the utility of numerous oxy-anions to catalyze GTP. The extended catalyst list from this family of oxy-anions included carboxylate, phenolate, sulfonate, phosphonate, sulfonamidate and perfluoroalkoxide. The list was further compounded by the ability to prepare a series of bi-anions from the stoichiometric reaction of the oxy-anions with their conjugate acids. Simple mono-oxyanionic salts such as tetrabutylammonium benzoate, are prepared, for example, by the reaction of aqueous tetrabutylammonium hydroxide with benzoic acid in a 1/1 mole ratio. This catalyst is soluble in polar solvents, THF, therefore a co-solvent is not required to maintain a homogeneous system.

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Molecular weight control and narrow polydispersities are achieved for the variety of oxy-anion catalysts. It has been noted however, that a number of parameters influence the activity of the catalysts. Firstly, the counterion is influential. It has been proposed that coordinating cations such as sodium in sodium acetate, complex strongly to the anion making the anion less available for interaction with the ketene silyl acetal functionality. Hence, in order to achieve more control over the polymerization process, the use of non-coordinating cations, like TAs and tetra(alkyl) ammonium, are recommended. In addition, preliminary investigation show that crown ethers complex to strongly coordinating counterions, like potassium, freeing the anion to serve as a GTP catalyst [98]. Secondly, the polymerization temperature appears to affect the catalytic activity of these catalysts. GTP is efficiently catalyzed at low temperatures (-78 °C) with bifluoride catalysts. Yet, it is only the most basic oxyanion catalysts, like acetates, that have been reported (within this class of compounds) to catalyze GTP at low temperatures. Certain oxyanion catalysts are ineffective for GTP at an appreciable rate at room temperature, although at elevated temperatures they become active catalysts [92].

The range of nucleophilic reagents which catalyze GTP permits the tailoring of the polymerization to selected reaction conditions, i.e., temperatures and solvents. The

level of catalyst required is calculated relative to the moles of the ketene silyl acetal initiator. It has been observed that nucleophilic catalysts levels less than 0.1 mole % relative to initiator are able to catalyze GTP . Electrophilic catalysts, e.g., zinc halides, are required at levels of ~10 mole% relative to monomer. Aluminum catalysts have been used at about 10 mole% based on initiator [93,99]. Although it has been proposed that the Lewis acid catalysts complex with the carbonyl oxygen of the incoming monomer [93], no reports have appeared indicating why such high concentrations of catalysts are required to polymerize the inherently much more reactive acrylate systems.

Electrophilic catalysts, like their nucleophilic counterparts, have been used in organic reactions involving silyl ketene acetals as illustrated in Table 7 [73,100-102]. The use of electrophilic catalysts to catalyze GTP has been limited in comparison to the many studies employing nucleophilic catalysts. These Lewis Acid catalysts; zinc halides, dialkylaluminum halides and dialkylaluminum oxide, do demonstrate more synthetic utility in the polymerization of alkyl acrylates than anion catalysts [68,93]. The reaction conditions must be more rigidly defined when employing Lewis acids to catalyze GTP. For example, donor solvents must be avoided during polymerization, with halogenated alkanes and aromatic hydrocarbons as the preferred solvents. The aluminum catalysts have been used

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Table 7. Organic Reactions of Silyl Ketene Acetals in the Presence of Electrophilic Catalysts

KETENE SILYL ACETAL	REAGENTS	PRODUCT	REF.
	 $\text{TiCl}_4, \text{CH}_2\text{Cl}_2$ -78 C		100
	 1) $\text{TiCl}_4 / \text{CH}_2\text{Cl}_2$ 2) H_2O		101
	 1) TiCl_4 & $\text{Ti}(\text{iPrO})_4$ 2) H_2O 3) C_2N_2		102
	 ZnBr_2		73

to catalyze GTP in acetonitrile with no apparent inhibitory effects; for example, Hertler, et al. [93], investigated the utility of various zinc halides. The best molecular weight control was observed with zinc iodide, while zinc chloride was poor. The crucial role of the polymerization temperature was also noted. Zinc halides effectively catalyze the GTP mechanism at room temperature, whereas aluminum catalysts are more sensitive. At ambient temperatures, an unexplained competitive decomposition reaction was observed with the aluminum catalysts. The complete polymerization of alkyl acrylates with aluminum catalysts at ambient temperatures was successful if a batch process was used. Polymerization rates of alkyl methacrylates at these temperatures is slow. By lowering the reaction temperature (-78 °C) the decomposition reaction is suppressed and GTP of acrylate monomers to high conversions results.

Whether the selected catalyst activates the initiator, polymer chain end or incoming monomer, transfer of the trialkylsilyl group results with the addition of a new monomer unit. Thus, after each monomer addition, a ketene silyl acetal fragment is generated. It is the formation of this fragment at the chain end which severely limits the choice of monomers that can undergo polymerization by GTP. A review of monomers that polymerize under the GTP reaction conditions will now be reviewed.

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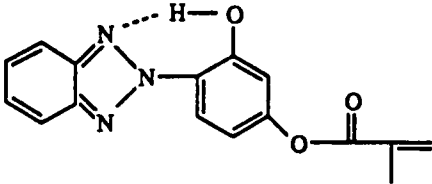
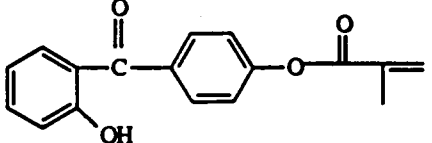
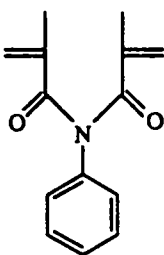
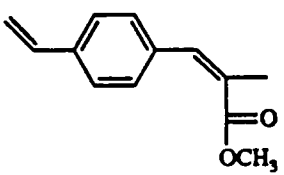
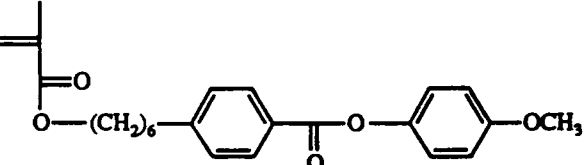
MONOMERS. GTP is more limited than anionic polymerization mechanisms in the breadth of monomers which can undergo this mode of polymerization. A range of monomers, polar and nonpolar, can be polymerized by anionic techniques if the monomer is capable of stabilizing the propagating carbanion. Monomers such as styrene and butadiene, which are polymerized anionically to high conversions even on a commercial level, cannot be polymerized by the GTP mechanism. The duPont patents list a vast array of monomers for GTP [67,103]. Various classes of monomers that are amenable to GTP include α,β -unsaturated esters, ketones, nitriles and carboxamides. These result in the preparation of poly(alkyl acrylate)s, poly(alkyl methacrylate)s, poly(acrylonitrile)s, poly (acrylamide)s and poly(maleimide)s. From the previous discussion pertaining to initiators and catalysts it is evident that under the appropriate reaction conditions, both alkyl methacrylates and alkyl acrylates can be polymerized to high conversion with controlled molecular weight and narrow polydispersities by GTP.

GTP, like anionic polymerization, is terminated by protic sources. Hence, monomers containing active hydrogens cannot be polymerized directly and reactive groups (such as the hydroxyl functionality of 2-hydroxyethyl methacrylate), must be protected prior to polymerization by either one of these living polymerization mechanisms. In some instances

the presence of phenolic hydroxyl protons does not appear to interfere with the GTP mechanism. The GTP mechanism has been elegantly applied by Gomez and Neidlinger [104,105] for the preparation of poly(methyl methacrylate) resins containing ultraviolet stabilizers, as shown in Table 8, which could serve as transparent, light stable acrylic resins to cover solar energy panels. Block copolymers were prepared by sequential addition of either 4-methacryloxy-2-hydroxybenzophenone or 2-(2-hydroxy-4-methacryloxyphenyl)-2H-benzotriazole to living PMMA followed by the addition of MMA. Though hydroxyl protons usually terminate GTP, it has been suggested that strong hydrogen bonding to the carbonyl or triazole groups prevent termination and hence, unprotected monomers can be copolymerized.

The list of monomers polymerizable by GTP is limited relative to anionic and free radical techniques. Nevertheless, a number of unique situations arise for the polymerization of unusual monomers. Table 8 lists some of the unusual monomers elegantly polymerized by GTP. Kozakiewicz et al. [106], was interested in the hydrolytic stability of poly(N,N-dimethylacrylamide) and also utilized GTP to prepare 6-membered ring containing imides. Other suitable monomers listed contain somewhat reactive pendent groups. Monomers containing allyl and sorbyl pendent ester functionalities lead to insoluble crosslinked products by free radical techniques yet, with GTP, the functional

Table 8. Unusual Monomers for GTP

ENTRY	MONOMER	REF.
1.		104,105
2.		104,105
3.		106
4.	ALLYL METHACRYLATE	67,103
5.	SORBYL METHACRYLATE	
6.	GLYCIDAL METHACRYLATE	
7.		107,109
8.	N-(ETHYL-3-HYDROXYETHYL)CARBOZYL METHACRYLATE	109
9.		110

pendent groups are inert during polymerization [67]. Monomers such as p-vinylbenzyl methacrylate [109] as well as glycidyl methacrylate [68,103] have been selectively polymerized using GTP, however the temperature of polymerization must be controlled to prevent the thermal free radical polymerization of some of these pendent functional groups.

Furthermore, the difference in the relative reactivity of acrylic and methacrylic ester monomers to the GTP mechanism provides a unique situation [67,68]. Acrylates polymerize at a much higher rate than methacrylates, allowing acrylic monomers bearing methacrylate functional groups to be selectively polymerized leaving behind unreacted pendent methacrylate functional groups, e.g., poly(methacryloxyethyl acrylate). This higher rate of polymerization for more polar monomers could potentially interfere in the preparation of random copolymers between the two families of monomers; alkyl acrylates and alkyl methacrylates. It is expected that a tapered block copolymer would result with the more reactive acrylate polymerizing to completion before any appreciable polymerization of the methacrylate monomer. Block and random copolymers have been cleanly prepared within the same monomer family and some investigators have reported the reactivity ratios for the statistical copolymerization of methyl methacrylate and n-butyl methacrylate [108].

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The ability to polymerize unusual monomers leads to the preparation of a variety of novel materials. Two different groups have polymerized monomers with mesogenic groups by GTP for the preparation of polymers having liquid crystalline characteristics. Pugh and Percec [107,109] prepared polymers containing both mesogenic and nonmesogenic electron-donor and electron-acceptor pendent groups. Using the GTP technique, they were able to study the variation of the glass transition temperature in liquid crystalline oligomers prepared from monomers like N-(2-hydroxyethyl)-carbazoyl methacrylate. In addition, Kreuder et al.[110], further examined the synthetic utility of GTP for the preparation of liquid crystalline poly(alkyl methacrylate)s (Table 8, entry 9) in comparison to LCPs prepared by free radical and anionic techniques. The LCPs prepared by GTP resemble the free radically prepared LCPs showing syndiotactic stereochemistry and nematic phase behavior. The anionic LCPs however were highly isotactic and tended to yield exclusively, highly ordered, smectic mesophase materials. Thus, by judicious choice of the polymerization method, LCPs with controlled liquid crystalline phase behavior can be prepared under controlled living polymerization conditions as evidenced by these investigations. The corresponding random copolymers of the mesogenic monomer with methyl methacrylate showed no

mesogenic behavior and hence did not lead to liquid crystalline polymers.

Other investigations involving the three polymerization mechanisms; anionic, free radical, and GTP have involved the polymerization of optically active and racemic mixtures of α -methylene- r -methyl- r -butyrolactone [111]. The free radical preparation of this monomer resulted in highly atactic polymers, while those prepared by anionic techniques, as well as by GTP, were highly isotactic. Further studies using chirally pure monomers led to limited amounts of isotactic polymer prepared by free radical methods. This indicated that the monomer itself influenced the tactic placement rendering the unusually high amount of isotactic stereochemistry observed for GTP polymers.

The application of GTP has been extended to the design of defined polymer architecture. The aforementioned monomers yield a variety of unusual homo-, block, graft and random polymers. In some cases pendant, reactive functional groups are present which can be, for example, reacted further to yield interpenetrating networks, or graft copolymers. As previously addressed, the use of protected initiators in combination with coupling reactions has led to the preparation of telechelic poly(alkyl acrylate)s and poly(alkyl methacrylate)s. Depending on the functionality of the material and co-reactants, these telechelic precursors can be utilized to prepare a variety of

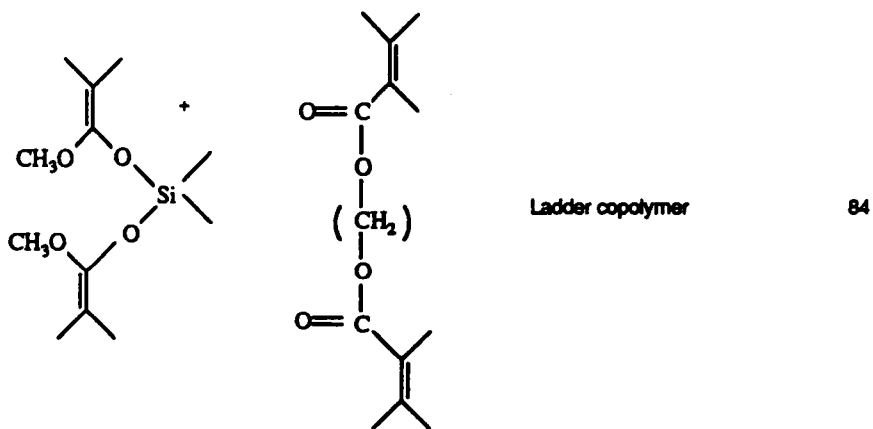
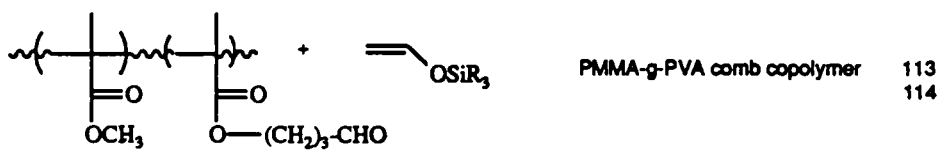
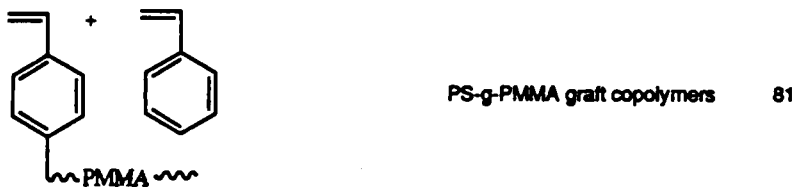
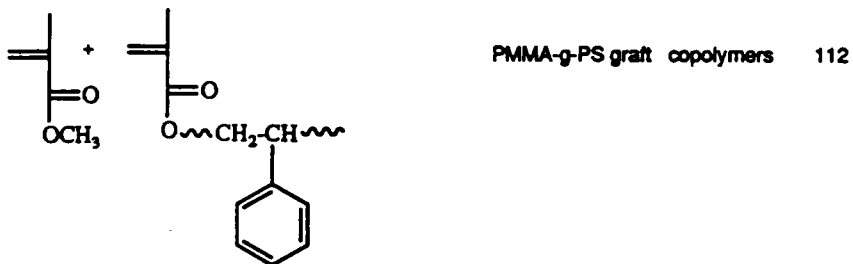
architectures including block and segmented systems. Extending the concept of functionalized polymers, GTP has been utilized in the preparation of macromonomers. The macromonomer technique enables the preparation of a polymer that has a single monomer unit at its chain end, which can undergo subsequent copolymerization yielding graft copolymers, with grafts of precisely controlled molecular weight. A number of graft copolymers have been prepared using the macromonomer technique and GTP in either synthesis of the graft [81] or backbone [112]. These are illustrated in Table 9. Also reported in Table 9 are monomers which can be polymerized to polymers having various architectures including ladders, stars and combs prepared by GTP [84] and aldol GTP [113,114].

GTP appears to be a versatile method of polymerization for selected families of monomers leading to polymers of controlled architecture; e.g. linear (homo- or block polymers) or branched (graft, star or ladder polymers). It provides routes to polymers containing functional pendent, chelic or telechelic groups. It is generally accepted that polymerization proceeds via transfer of the trialkylsilyl group from the initiator or propagating chain end to the incoming monomer unit in the presence of a catalyst. Yet, many questions have risen to confirm the actual transfer mechanism. The following section will review the

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Table 9. Some Appropriate Monomers and Various Copolymer Architectures Accessible Via GTP

REACTANTS FOR GTP COPOLYMERIZATION RESULTING ARCHITECTURE REF.



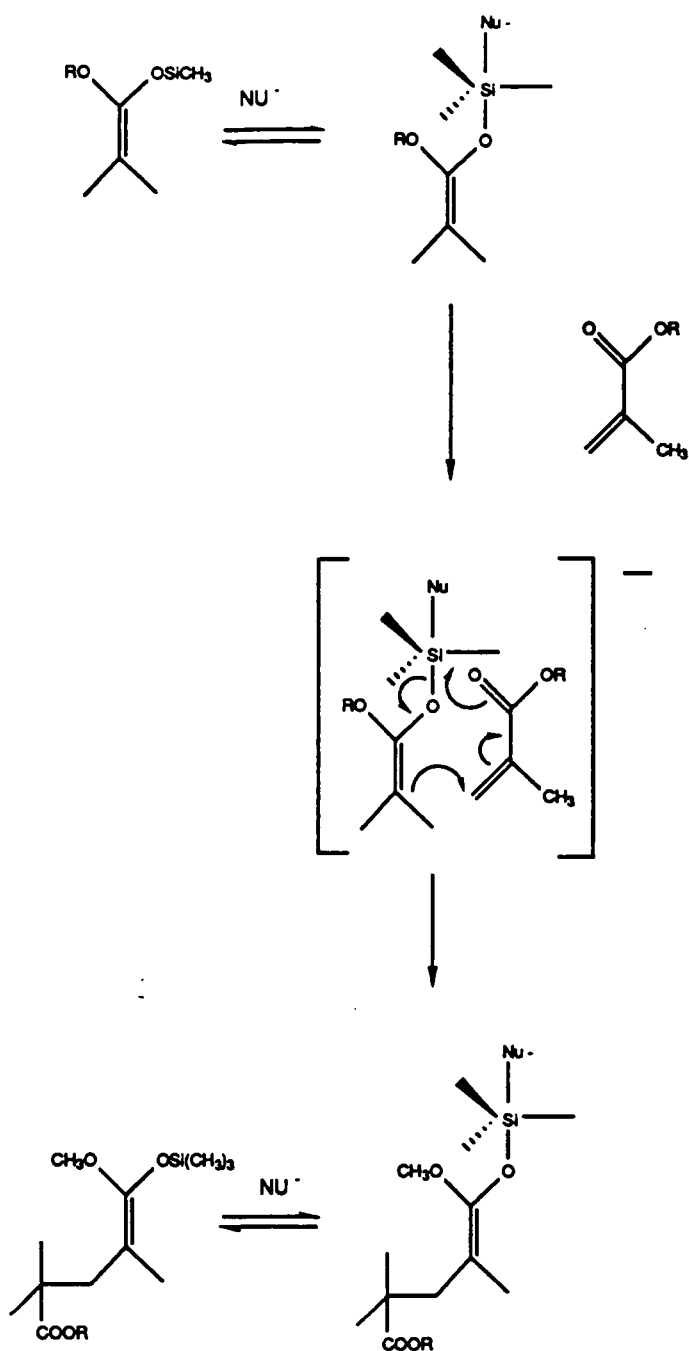
investigations that have been carried out to elucidate the mechanism of GTP.

GTP:MECHANISTIC STUDIES

INTRODUCTION. Based on mechanistic studies using trapping and labeling techniques, Webster et al., [66,67] proposed an intermolecular transfer mechanism for GTP, in which the silyl group is directly transferred from the initiator or propagating chain end to the carbonyl oxygen of the monomer via a hypervalent silicon intermediate. Scheme 7 illustrates the activation of the silicon atom by a nucleophile, followed by the formation of the hypervalent silicon intermediate in the presence of monomer and the concerted electron rearrangements that lead to transfer of the trialkylsilyl group. Despite the report that fluorosilane was not formed in a reversible dissociative step and silyl group exchange is not involved, detailed aspects of the GTP mechanism are not yet well elucidated.

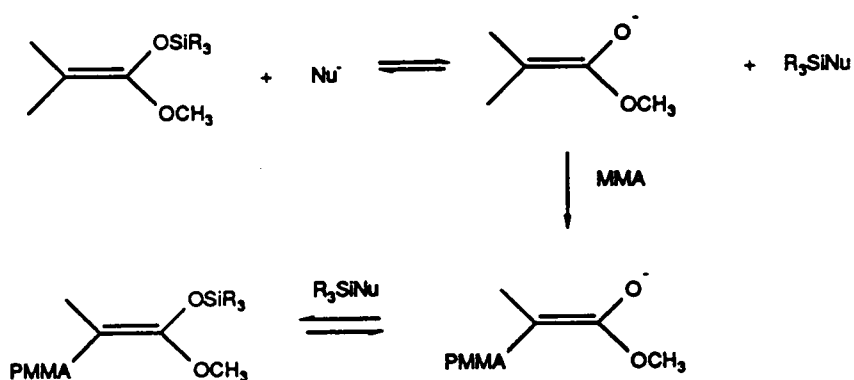
ASSOCIATIVE VS DISSOCIATIVE MECHANISMS. Several mechanisms have been proposed for GTP. The principal mechanistic question that was addressed by duPont workers was whether GTP took place via a dissociative or associative mechanism [115,116]. Schemes 8 and 9 illustrate two

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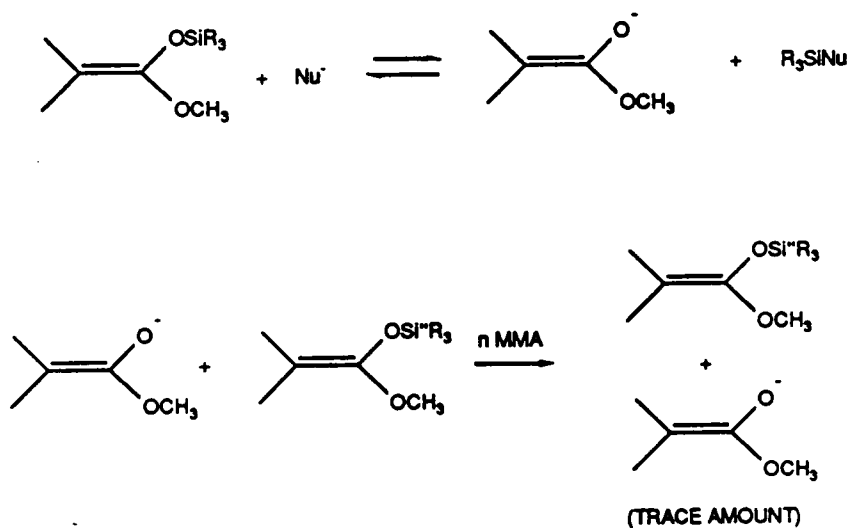
115. Sogah, D.Y.; Farnham, W.B. In Organosilicon and Bioorganosilicon Chemistry; Sakurai, H. Ed.; John Wiley & Sons: New York, 1985; Chapter 20.

Scheme 7. Associative Mechanism for GTP



115. Sogah, D.Y.; Farnham, W.B. In Organosilicon and Bioorganosilicon Chemistry; Sakurai, H. Ed.; John Wiley & Sons: New York, 1985; Chapter 20.

Scheme 8. Reversible Dissociative Mechanism for GTP



115. Sogah, D.Y.; Farnham, W.B. In Organosilicon and Bioorganosilicon Chemistry; Sakurai, H. Ed.; John Wiley & Sons: New York, 1985; Chapter 20.

Scheme 9. Irreversible Dissociative Mechanism for GTP

possible dissociative mechanisms. The first Scheme represents a reversible dissociative mechanism in which the nucleophile reversibly cleaves the trialkylsilyl group from the initiator generating the ester enolate. The ester enolate is the propagating species, which, upon repeated addition of monomer, yields a polymeric carbanion. Upon resilylation, the ketene trialkylsilyl acetal fragment is regenerated at the polymer chain end. The other dissociative mechanism is similar, however, the trialkylsilyl group is irreversibly cleaved from the initiator. The ketene silyl acetal fragment is regenerated at the chain end by other silyl ketene acetals. The associative mechanism, illustrated in Scheme 7, involves the direct transfer of the silyl group from the initiator or propagating chain end to the incoming monomer unit via a hypervalent silicon intermediate. All three mechanisms ultimately result in the presence of a ketene silyl acetal fragment at the chain end. The existence of this moiety was confirmed using ^{13}C NMR and capping reactions [78,115]. Recognizing however, that the important distinction between the mechanisms exists with the trialkylsilyl group, Farnham and Sogah set out to dismiss the two dissociative mechanisms.

In the associative mechanism the trialkylsilyl group is not exchanged between chains; i.e. the identity of the silicon atom remains invariant throughout the

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polymerization. Under GTP reaction conditions, the formation of fluorosilanes in a reversible, dissociative step (Scheme 8) was dismissed by labelled silyl fluoride exchange experiments using catalyst quenchers such as spiro silanes and silver nitrate [115,116].

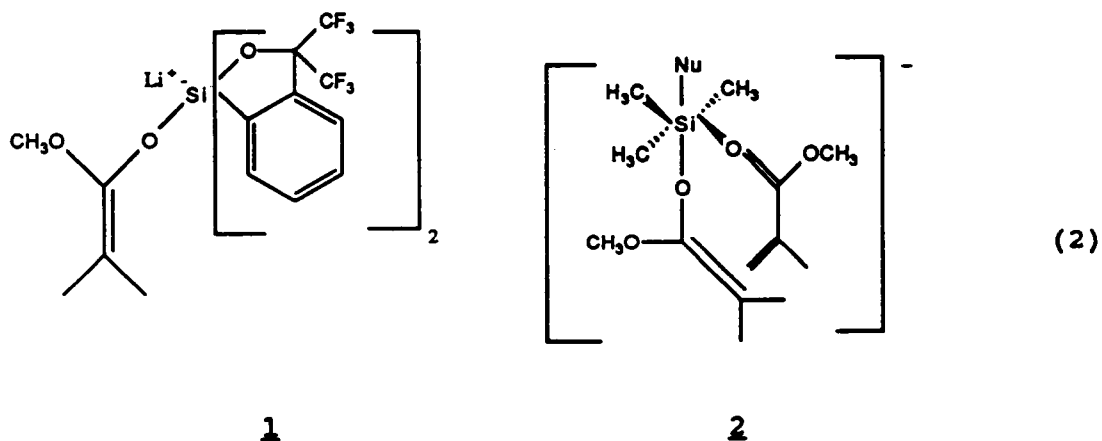
Other results however, reveal that living oligomers and silyl ketene acetals exchange silyl groups in the presence of a nucleophilic GTP catalyst. This indicates that the resilylation of ester enolates by other silyl ketene acetals (monomeric or oligomeric), may be facile and pronounced at early stages of the reaction. More importantly, it was observed that no silyl group exchange between living oligomeric species occurred. Using two "living" homopolymers polymers of poly(methyl methacrylate) and poly(n-butyl methacrylate), double labelling experiments were performed to address this mechanistic question concerning the difference between the relative rates of silyl group exchange and intermolecular transfer during propagation [115,116].

It was shown that silyl group exchange does not occur between living PMMA and living poly(n-butyl methacrylate) (PnBMA) chain ends, which supports an "intermolecular" silyl transfer mechanism (Scheme 7). The double labelling experiments were however, inconclusive for the dismissal of the irreversible dissociative route. Though competition between the propagation rate and rate of silyl group

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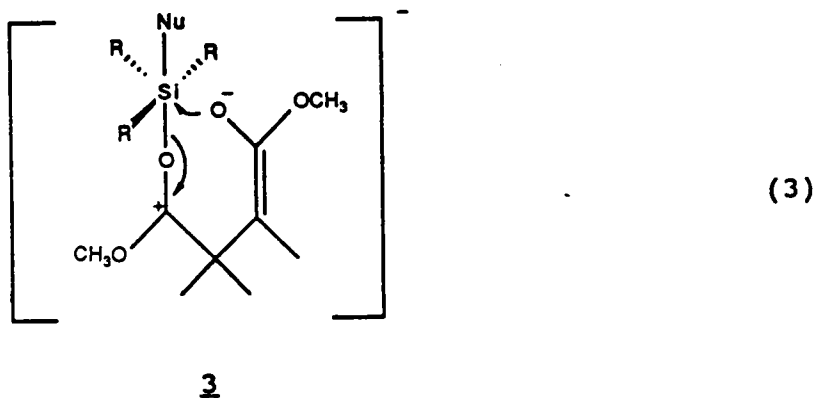
exchange between initiator and living oligomers may be evident, it was concluded that the mechanism of propagation is independent of the degree of polymerization and changes in the mechanism of polymerization are inconsistent with the fact that the initiator controls the molecular weight.

Further support for the associative mechanism of polymerization was found in model studies. Silicon differs from carbon in its ability to expand its valence shell and form five and six coordinate compounds [117-119]. Supportive evidence for the involvement of pentacoordinate silicon species in GTP was determined from the polymerization of MMA by a stable pentacoordinate silicate (1) [115]. Neither dissociative mechanism proposes a pentacoordinate intermediate. Although the ligands of 1 and the hypervalent hexacoordinate intermediate 2 are different, the results suggest activation of the initiator is necessary in GTP (2).

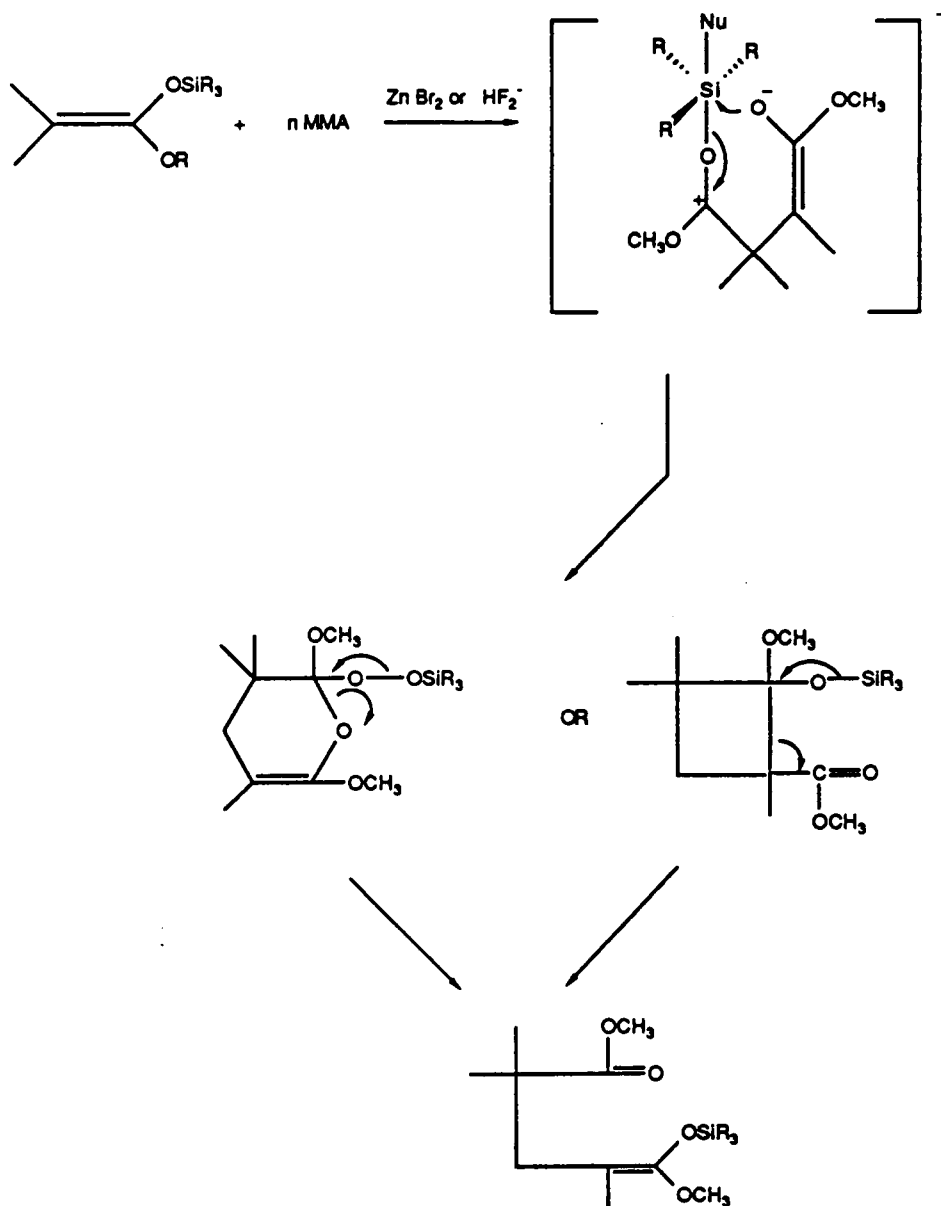


Based on this information, labelling studies and model compounds, the exclusive operation of the two dissociative mechanisms was eliminated in favor of the proposed associative mechanism in which monomer adds through a concerted transition state involving coordination to the silicon (structure 2). Note that these studies appear to have been conducted with only one of the possible families of catalysts.

In a recent review, Webster also suggests that an alternative transition state may be involved [68]. The proposed transition state involves two steps, with carbon-carbon bond formation as the first event after coordination of catalyst to silicon (structure 3).



In addition it was proposed that intermediates (4) and (5) may intercede prior to silyl transfer (Scheme 10). Though this additional step in the pathway is purely speculative, it does unify the mechanism of GTP with respect to electrophilic and nucleophilic catalysts. Further studies



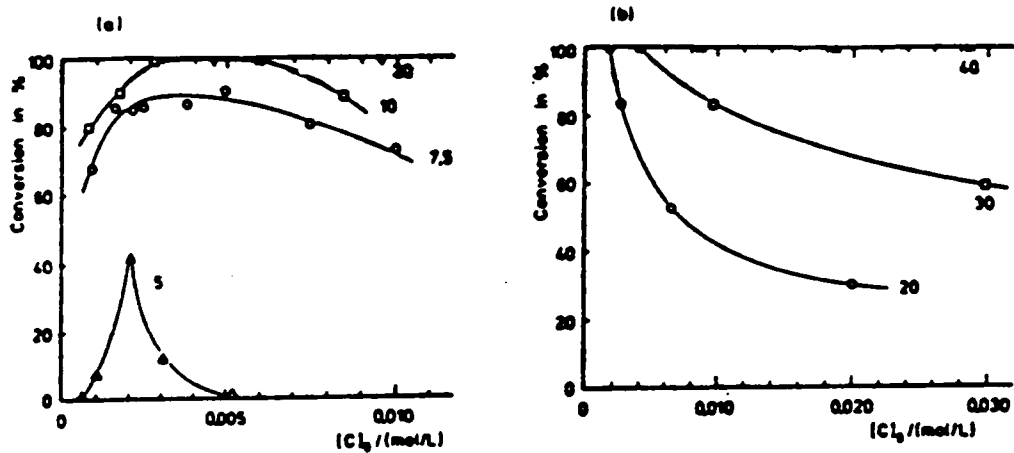
68. Webster, O.W.; Sogah, D.Y. In Recent Advances In Mechanistic and Synthetic Aspects of Polymerization; Fontanille, M., and Guyot, A., Eds.; NATO ASI Series 215; D. Reidel Publishing: Dordrecht, Holland. 1987; pp. 3-21.

Scheme 10. Unifying Pathway for GTP with Nucleophilic or Electrophilic Catalysts

to elucidate the nature of the intermediates present in the associative mechanism of GTP have involved the studies examining the role of the catalyst as well as the kinetics of polymerization. These investigations will be summarized in the following sections.

INITIATOR TO CATALYST RATIO. Kinetic investigations utilized to elucidate the mechanism of GTP have been rather limited, yet, a number of unusual anomalies have been disclosed by examining the role of the catalyst. Banderman et al. [85,87,88,91,120,121], have published a series of kinetic results for the group transfer polymerization of MMA in which the ratio of initiator to catalyst was systematically varied. The initial investigations were carried out in acetonitrile with trimethylsilyl cyanide as the initiator and $\text{TASF}_2\text{SiMe}_3$ as the catalyst (documented as co-initiator) [85]. Their results indicate that the concentration of catalyst influences the degree of control achieved in the polymerization. It was reported that for a given initiator concentration, the conversion to polymer, and molecular weight of the final polymer both go through a maximum as the catalyst concentration is increased (Figure 1 & 2) [85]. The effect of the initiator to catalyst concentration was unclear due to the observed induction period. The induction period noted was attributed to the complexation of catalyst and

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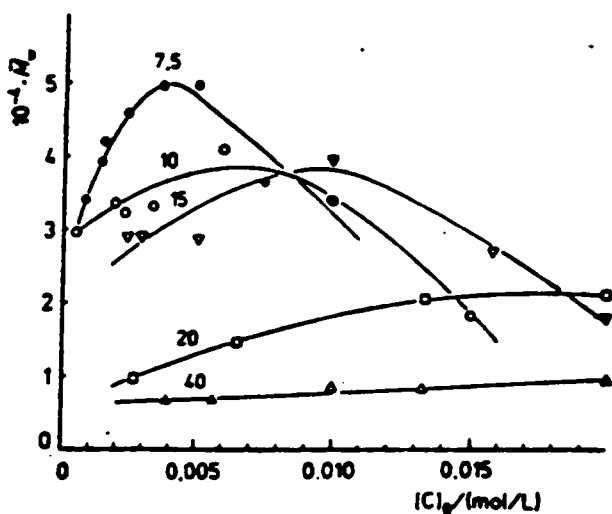


Maximum conversions in the polymerization of methyl methacrylate (MMA) with trimethylsilyl cyanide (I) in acetonitrile at 293 K versus initial catalyst concentration $[C_1]$ (a) for $N(C_2H_5)_4CN$ (b) for $TASF_2SiMe_3$. Numbers at the curves denote $[I]_0$ in mmol/L.

85. Bandermann, F.; Speikamp, H.D. Makromol. Chem., Rapid Commun. 1985, 6, 335-339.

Figure 1. Conversion vs. Initial Catalyst Concentration.

Weight-average molecular weight (\bar{M}_w) versus initial catalyst concentration $[C]_0$ in the polymerization of methyl methacrylate (MMA) with trimethylsilyl cyanide (I) and $N(C_2H_5)_3CN$ (C) in acetonitrile at 293 K. $[MMA] = 1.83 \text{ mol/L}$; numbers at curves denote $[I]_0$ in mmol/L



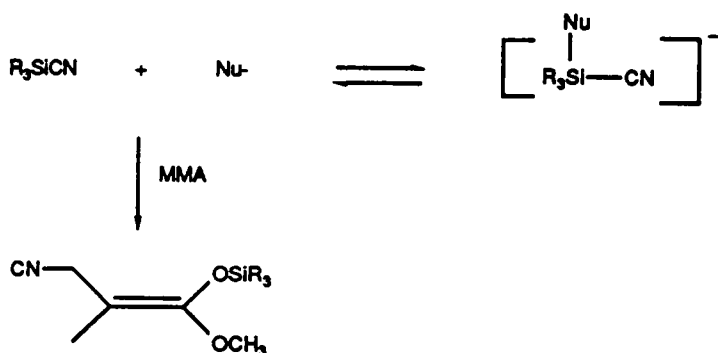
85. Bandermann, F.; Speikamp, H.D. Makromol. Chem., Rapid Commun. 1985, 6, 335-339.

Figure 2. Molecular Weight vs. Catalyst Concentration

initiator. It was proposed that the initiator complexed the catalyst more strongly than the propagating chains, and therefore, until the trimethylsilylcyanide initiator is consumed by addition to monomer forming an active ketene silyl acetal, a slower polymerization rate is observed as an induction period (Scheme 11) [68].

In order to disclose the effect of catalyst concentration on the mechanism of GTP, investigations continued with an expanded initiator and catalyst set [87,88,91,120,121]. Kinetic experiments, using either $\text{TASF}_2\text{SiMe}_3$ or tetraethylammonium cyanide (Et_4NCN) in combination with either trimethylsilyl cyanide or [(1-methoxy-2-methyl)-1-propenyloxy]trimethylsilane (MTS), were performed in acetonitrile [87,120,121]. In all cases the GTP of MMA deviated from a living system. Thorough investigations using chromatographic techniques and NMR resolved the side reactions causing deviations from living behavior [120].

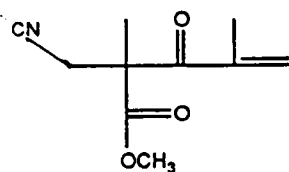
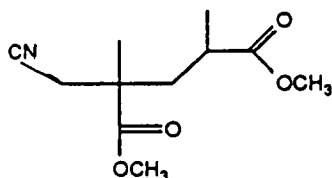
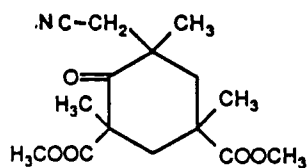
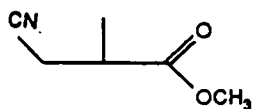
Focusing on the GTP of MMA using MTS as the initiator and Et_4NCN as the selected catalyst, the first side reactions detected were attributed to the anionic oligomerization of MMA by the catalyst, Et_4NCN . This addition reaction of monomer with catalyst results in a loss of "active" catalyst for polymerization. Sitz et al., [120] resolved a number of species using chromatographic techniques, which are illustrated in Table 10. Species 3



85. Bandermann, F.; Speikamp, H.D. *Makromol. Chem., Rapid Commun.* 1985, 6, 335-339.

Scheme 11. Proposed Interaction between Cyanide based Initiators and Fluoride Catalysts

Table 10. Identified Species in GTP from the Presence of Acetonitrile



120. Sitz, H.D.; Speikamp, H.D.; Bander mann, F. Makromol. Chem. 1988, 189, 429-435.

can be recognized as a well known termination product in the anionic polymerization of MMA. Further studies, confirmed by NMR, elucidated side reactions involving the MTS initiator. These side reactions involved the isomerization of MTS to its carbon silylized form. Furthermore, both of these species react with acetonitrile via an exchange reaction in the presence of nucleophilic catalyst to generate $\text{Me}_3\text{SiCH}_2\text{CN}$ and methyl isobutyrate. Since the active chain ends have the same structure as MTS, according to the proposed associative mechanism, it is assumed that severe termination can occur in GTP due to this exchange. This results in the loss of active centers, so complete conversion and molecular weight control cannot be obtained under all experimental conditions. Finally, it was determined that MTS could react with Et_4NCN forming trimethylsilylcyanide, an initiator for GTP.

Further support for these side reactions was elucidated with the trimethylsilyl cyanide/ $\text{TASF}_2\text{SiMe}_3$ and trimethylsilyl cyanide/ Et_4NCN systems [91]. Though $\text{TASF}_2\text{SiMe}_3$ does not undergo oligomerization reactions with MMA in acetonitrile, both catalysts, $\text{TASHF}_2\text{SiMe}_3$ and Et_4NCN , show similar behavior with respect to initiation and propagation reactions, and to the termination reaction of propagating chains with the solvent. It was concluded from these studies, that the living character of GTP in acetonitrile depends strongly on the catalyst concentration.

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At high initiator concentrations and low catalyst concentrations, the propagation reaction is faster than termination reactions. At higher catalyst concentrations, the termination reactions become dominant, limiting the maximum conversion, molecular weight and causing an apparent broadening of the molecular weight distribution.

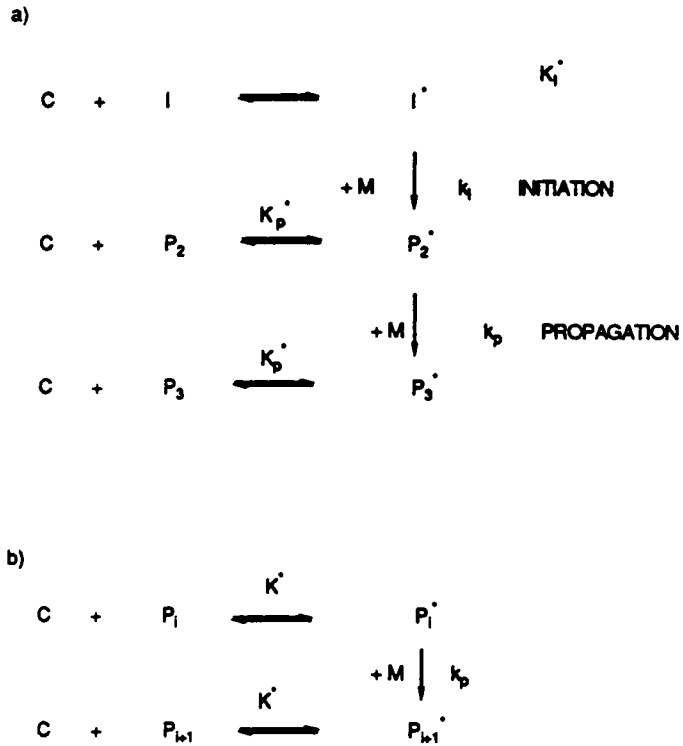
To further examine the effect of catalyst activity on GTP, Sitz and Bandermann selected catalysts that would not require the use of acetonitrile, hence reducing the termination reactions between solvent and initiator or propagating chain ends [91]. THF soluble catalysts tris-(piperidino)sulfonium difluorosilicate ($\text{TPSF}_2\text{SiMe}_3$), tris-(piperidino)sulfonium bifluoride (TPF_2H) and tetrabutylammonium cyanide (tBu_4NCN) were studied. In all cases, the catalysts concentrations necessary for rapid GTP of MMA are extremely low and the reaction rate was observed to increase with increasing catalyst concentrations. Though it was reported that molecular weight was nearly independent of catalyst concentration indicating a living system, side reactions were observed in each catalyst system. TPF_2H , for example, not only promoted the isomerization of MTS to its carbon silylized product, but promoted the oligomerization of MTS to an ester and releasing Me_3SiF . Consequently, the number of active centers are reduced causing deviations from living behavior. For these reasons the tBu_4NCN system was examined. This

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catalyst is less active in the oligomerization of MTS, however it is known that cyanide anions can initiate the polymerization of MMA. It was determined that neither of these side reactions occur to any appreciable extent during the GTP of MMA and hence, they can be neglected under these reaction conditions.

These studies have focused on a systematic evaluation of the molar ratio of initiator to catalyst. From these investigations a number of unusual anomalies have been revealed that cause deviation in GTP from living behavior. Subsequently, it has been surmised that acetonitrile is an unacceptable solvent for GTP. In addition, $t\text{Bu}_4\text{NCN}$ has been proposed as an acceptable nucleophile for GTP.

KINETIC SCHEME. The focus of these studies just addressed has not elucidated any information about intermediates involved in the associative GTP mechanism. To gain deeper insight into the mechanism, Müller et al. [122-125], have probed the mechanistic questions through kinetic investigations. Their aim was to determine the reaction order with respect to the concentration of reagents of polymerization; monomer, catalyst, and initiator. Assuming the rate of propagation is faster than the rate of termination, Mai and Müller proposed a kinetic scheme consistent with the duPont associative mechanism (Scheme 12a) [123,124]. Noting that initiator and living chain end



I = Initiator
 I* = Activated Initiator
 P₁ = "Dormant" Polymer
 P₁* = "Activated" Polymer
 C = Catalyst
 M = Monomer

123. Mai, P.M.; Müller, A.H.E. Makromol. Chem., Rapid Commun. 1987, 8, 99-107.

Scheme 12. Kinetic Scheme For GTP Associative Mechanism

have the same structure the kinetic scheme is simplified (Scheme 12b). Passing over the detailed derivation of the kinetic equations, which can be found in references 123 and 124, the change in monomer concentration for a living system with time for this kinetic scheme can be written as Equation 1.

$$\ln([M]_0/[M]) = k_p \cdot [P^*] \cdot t = k_{app} \cdot t \quad \text{Eq. 1}$$

where

$$k_{app} = k_p \cdot \frac{K^* \cdot [I]_0}{1 + K^* \cdot [I]_0} \cdot [C]_0 \quad \text{Eq. 2}$$

$$= \text{const} \cdot [I]_0^\beta \cdot [C]_0 = k_p' \cdot [C]_0 \quad \text{Eq. 3}$$

For the above kinetic scheme, the important factor to note is the parameter β . The value of β corresponds to two limiting cases which are represented by (4). If the



equilibrium is shifted to the right hand side, represented by the pentacoordinate complex, which will also be addressed as activated (*), then the product of $(K^* \cdot [I]_0)$ is much greater than 1, hence; the concentration of activated species $[P^*]$ is equal to the concentration of catalyst $[C]_0$. The apparent rate constant subsequently reduces to equation 4.

$$\text{and } K^* \cdot [I]_0 \gg 1 \text{ then } \beta = 0 \quad \text{Eq. 4}$$

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$$k_{app} = k_p \cdot [C]_0 = k_p' \cdot [C]_0$$

Rearranging equation 4, the "pseudo" rate constant (k_p') equals the true rate constant (k_p). Alternatively, if the equilibrium shifts to the uncomplexed state, i.e. the left-hand side, then the product of ($K^* \cdot [I]_0$) is much less than 1, hence;

$$[P^*] = K^* \cdot [I]_0 \cdot [C]_0 \quad \text{Eq5.}$$

In turn, the apparent rate constant reduces to equation.

$$K^* \cdot [I]_0 \ll 1 \text{ then } \beta = 1 \text{ and} \quad \text{Eq6.}$$

$$k_{app} = k_p \cdot K^* \cdot [I]_0 \cdot [C]_0$$

Rearranging equations 2 and 3 for this limiting case the "pseudo" rate constant is a function of the initial initiator concentration (Equation 7)

$$k_p' = k_{app}/[C]_0 = k_p \cdot K^* \cdot [I]_0 \quad \text{Eq7.}$$

The apparent rate constant is dependent on the value of β , which may lie between zero and unity depending on the activation equilibrium of initiator or growing chains.

In summary, if GTP follows the kinetic scheme proposed by Mai and Müller, then it was predicted that the reaction order is first order with respect to monomer and catalyst, whereas the kinetic order with respect to initiator, β is expected to be $0 \leq \beta \leq 1$. This dependence of reaction

order on the rate of propagation has been defined by Equation 8 .

$$R_p = \text{const} \cdot [M]^\alpha \cdot [I]_0^\beta \cdot [C]_0^\tau$$

where $\alpha = 1$, $0 < \beta < 1$, and $\tau = 1$

$\epsilon \gamma^8 \phi$

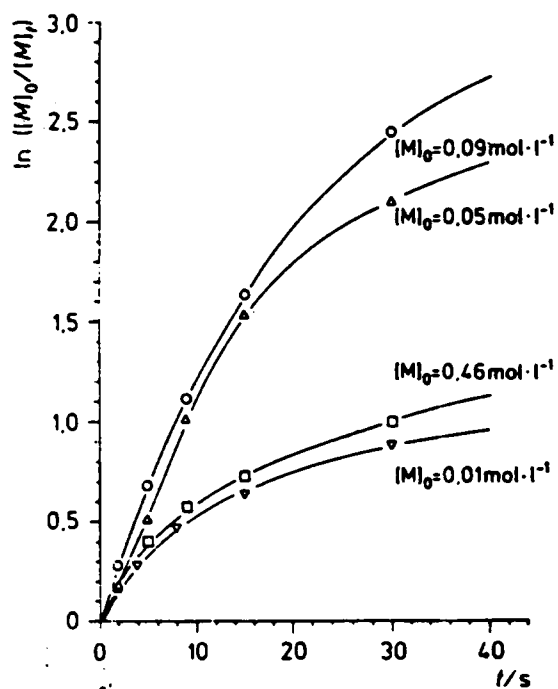
Kinetic investigations were executed to elucidate the reaction order with respect to the polymerization reagents. The results will be presented in the forthcoming sections with respect to each reagent; monomers, catalysts and initiator, as well as polymerization temperature. An important detail to note is the order of addition of the reagents employed in these studies. For all of the experiments, a solution of catalyst in THF (without acetonitrile) was charged to a premixed solution of the monomer and the initiator in THF. The order of addition is predicted to influence the results and hence, becomes a factor in the conclusions stated by Müller et al. [124,125].

EFFECT OF MONOMER CONCENTRATION. The kinetic scheme, described above, predicts a linear dependence with respect to monomer concentration. Müller et al. investigated the reaction order dependence with respect to two different alkyl methacrylates; methyl methacrylate and t-butyl methacrylate. For the GTP of both monomers using TASHF₂ as the selected catalyst and MTS as the initiator, it was reported that the kinetic order (α) observed is first order

with respect to monomer concentration (Figure 3). Variations from ideal living behavior were noted in the first order time-conversion plots. Deviations from linearity were observed in the latter stages of the polymerization of MMA, indicating the presence of termination reactions [122,123]. The deviations were much more pronounced for t-butyl methacrylate, rendering the determination of rate constants difficult. The higher extent of termination for TBMA was proposed to be attributed to the lower polymerization rate constant (k_p TBMA < k_p MMA by a factor ca. 2) [124,125]. The effect of temperature will be addressed in a preceding section since it provides valuable mechanistic information, but first the effect of catalyst and initiators concentrations will be addressed.

EFFECT OF CATALYST CONCENTRATION. Müller and his colleagues have generated a significant amount of information regarding TASHF₂ as the selected catalyst and some details using a variety of benzoate anions have been reported [122-125]. It is important to reiterate here that acetonitrile was not employed in the polymerizations involving TASHF₂; hence deviations from linearity were not directly attributed to side reactions documented by Bandermann et al.

The propagation reaction for GTP was predicted to be first order with respect to catalyst concentration. Two

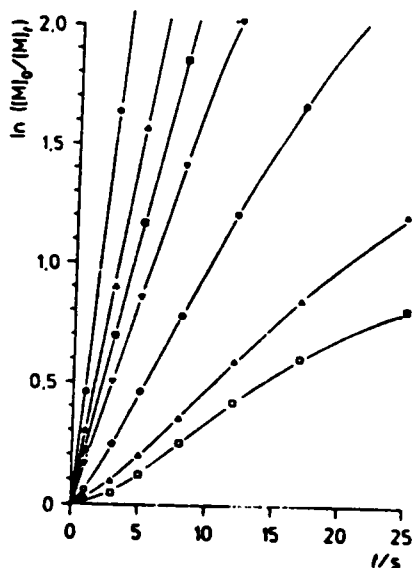


122. Mai, P.M.; Müller, A.H.E. Makromol. Chem., Rapid Commun. 1987, 8, 247-253.

Figure 3. Kinetic Order with Respect to MMA Concentration in the Presence of MTS and TASHF₂

plots are reprinted to demonstrate more effectively the effect of catalyst concentration on the polymerization rate [96]. The first order time conversion plots for the polymerization of MMA indicated that as the catalyst concentration was reduced, the apparent rate of polymerization decreased (Figure 4). At lower catalyst concentrations, slight induction periods were observed prior to the linear increases in reaction rates. Also noted, were the presence of termination reactions. The linearity of the bilogarithmic plot (Figure 5) with a slope of 1.17 indicates that the reaction order with respect to TASHF₂ catalyst is one, as predicted from the kinetic scheme (Scheme 12A).

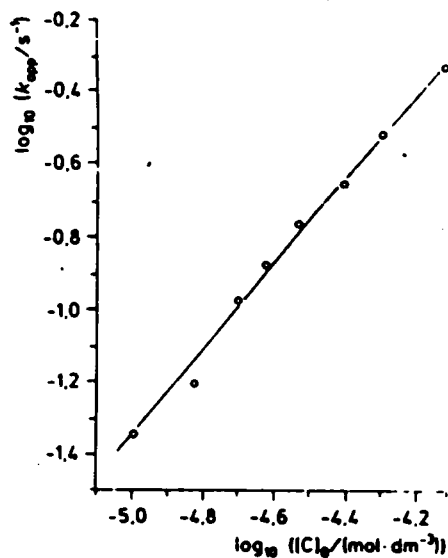
It was also reported that the "pseudo" rate constants (k_p') for the catalyst concentrations having induction periods, calculated from equation 3, were smaller than expected. Two probable explanations were accounted [123,124]. First, deactivation of the active centers during the induction period would decrease the k_p' from the calculated value. This explanation will be addressed in further detail when the order with respect to initiator concentration is addressed. In a private communication to Müller et al., duPont workers disclosed that a kinetic order of 2 for the initial stage of polymerization (oligomerization to trimers) was found [124]. They reportedly attributed this to a pre-equilibrium of fluoride



First-order time-conversion plots for group transfer polymerization of methyl methacrylate with 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene and tris(dimethylamino)sulfonium bifluoride in tetrahydrofuran as a function of catalyst concentration; ● = run 44, ▲ = run 45, ■ = run 46, ▼ = run 47, ○ = run 48, △ = run 49, □ = run 50 (for experimental conditions cf. Tab. 1)

123. Mai, P.M.; Müller, A.H.E. Makromol. Chem., Rapid Commun. 1987, 8, 99-107

Figure 4. First Order Conversion vs Time Plots for various of concentrations of TASHF₂



Bilogarithmic plot of the apparent rate constants k_{app} vs. catalyst concentrations for group transfer polymerization of methyl methacrylate with 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene and tris(dimethylamino)sulfonium bifluoride in tetrahydrofuran (runs 44–50 and run 38, cf. Tab. 1). Slope equal to 1,17

123. Mai, P.M.; Müller, A.H.E. Makromol. Chem., Rapid Commun. 1987, 8, 99–107.

Figure 5. Bilogarithmic Plot of k_{app} vs Concentration of TASHF₂

ions from bifluoride. It was cited that this may be related to the observed induction period.

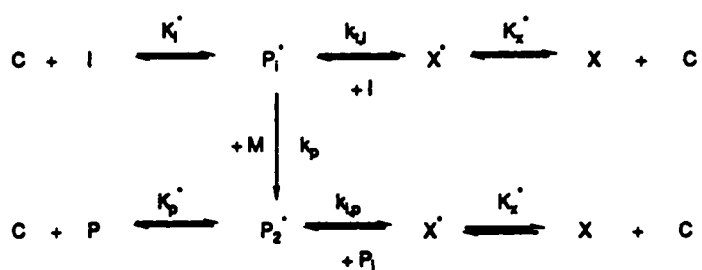
Initial results were reported for the polymerization of MMA with TAS benzoate [125]. Though the reaction order with respect to monomer was again first order, the order with respect to catalyst concentration was reported to be in a range between -0.3 and +1.0, depending on reaction conditions and catalyst nature. More details of this particular system will be addressed with regard to the initiator concentration in the next section.

EFFECT OF INITIATOR CONCENTRATION. For the defined kinetic scheme, the reaction order (β) with respect to the initiator concentration was cited to be very influential in defining the relationship of the true rate constant (k_p) to the "pseudo" rate constant (k_p'). It was defined above that the value of β varied between zero and unity depending on the activation equilibrium between dormant polymer chains and activated polymer chains (4).

In order to gain more insight into the activation equilibrium, the influence of the initiator concentration was studied [123,124]. The influence of the concentration of 1-methoxy-1-(trimethylsilyloxy)-2-methyl-1-propene (MTS) was reported for two different nucleophilic catalysts; bifluoride and oxyanion. For the polymerization of MMA in the presence of TASHF₂, the first order time-conversion

plots were characterized initially by slight induction periods when high initiator concentrations are employed [123]. Linearity was observed with slight non-linearity at longer times and was attributed to the termination of growing chains. Using a bilogarithmic plot, the reaction order was determined to be -0.27 , which was not consistent with the defined kinetic scheme (Scheme 12A). According to Mai and Müller, this negative order dependence conceivably indicates that the initiator is inhibiting the reaction, hence; they revised the original kinetic scheme to account for this anomaly (Scheme 13) [123]. According to this scheme, an inactive species is generated that is capable of binding to the catalyst resulting in lower apparent rate constants. It was proposed that the induction periods observed may be related to this phenomenon.

As mentioned in the previous section, the polymerization of MMA using TAS benzoate was reported [125]. Though the reaction order with respect to catalyst was not explicitly defined, a reaction order of unity with respect to MTS concentration was documented. This indicated that the activation equilibrium was shifted to the left-hand side (4), hence; it was sighted that because fewer activated species are considered to be present at any given time, the reaction was proposed to be considerably slower than for the bifluoride catalyst system. The rate constants for propagation could not be accurately determined since



123. Mai, P.M.; Müller, A.H.E. Makromol. Chem., Rapid Commun. 1987, 8, 99-107.

Scheme 13. Revised Kinetic Scheme

equilibrium constants (K^*) were not known and because of the ambiguous behavior of reaction order with respect to the catalyst concentration.

EFFECT OF TEMPERATURE. Muller et al. [122,124], continued investigations by examining the temperature dependence of rate constants in THF using $TASHF_2$ for the GTP of MMA and tBMA. The temperature range examined spanned from ambient to -82 °C. To avoid induction periods, all of the experiments of the temperature study were performed at fairly high catalyst levels. For the GTP of MMA, induction periods became evident as the temperature was decreased, although as the propagation rate increased, ideal first order behavior was observed leading to complete monomer conversion [122,124]. For tBMA, "induction periods" were not observed except at temperatures below -20 °C, however termination was much more evident at ambient temperatures rendering the determination of rate constants difficult [124]. Note that this may be related to residual t-butanol present from the synthesis of the monomer.

From the maximum slopes of the first order time-conversion plots (k_{app}) and assuming $K^* \cdot [I]_0 \gg 1$ based on the reaction order with respect to initiator ($\beta=0$) the rate constants were calculated. If the assumption $K^* \cdot [I]_0 \gg 1$

does not hold the reported data does represent the lower limit of the rate constants from Equation 9.

For the general case ($0 < \beta < 1$)

$$k_p' = k_p \cdot \frac{K^* \cdot [I]_0}{1 + K^* \cdot [I]_0} < k_p \quad \text{Eq. 9}$$

From the temperature study, an Arrhenius plot was constructed for the determination of the energy of activation (E_a) and frequency factor (A). For both monomers, the Arrhenius plot was linear yielding direct evidence for the existence of only one active species during polymerization [25,124]. Müller directly compared the E_a and $\log A$ of these two monomers polymerized by GTP to the values obtained by anionic polymerization in THF with different counterions. Table 11 displays these values and the similarity indicates parallel mechanisms for the two processes. For the associative mechanism proposed by Webster et al., it was cited that the coordination of carbonyl group of the approaching monomer to the hypervalent silicon atom would require much higher activation entropies [122,124]. This translates into lower frequency exponents. Based on the activation parameters, it was proposed by Müller et al., [122,124] that monomer addition is more likely a two step process. That is, the rate determining step is the addition of a vinyl group to the activated initiator or chain end. This process is subsequently

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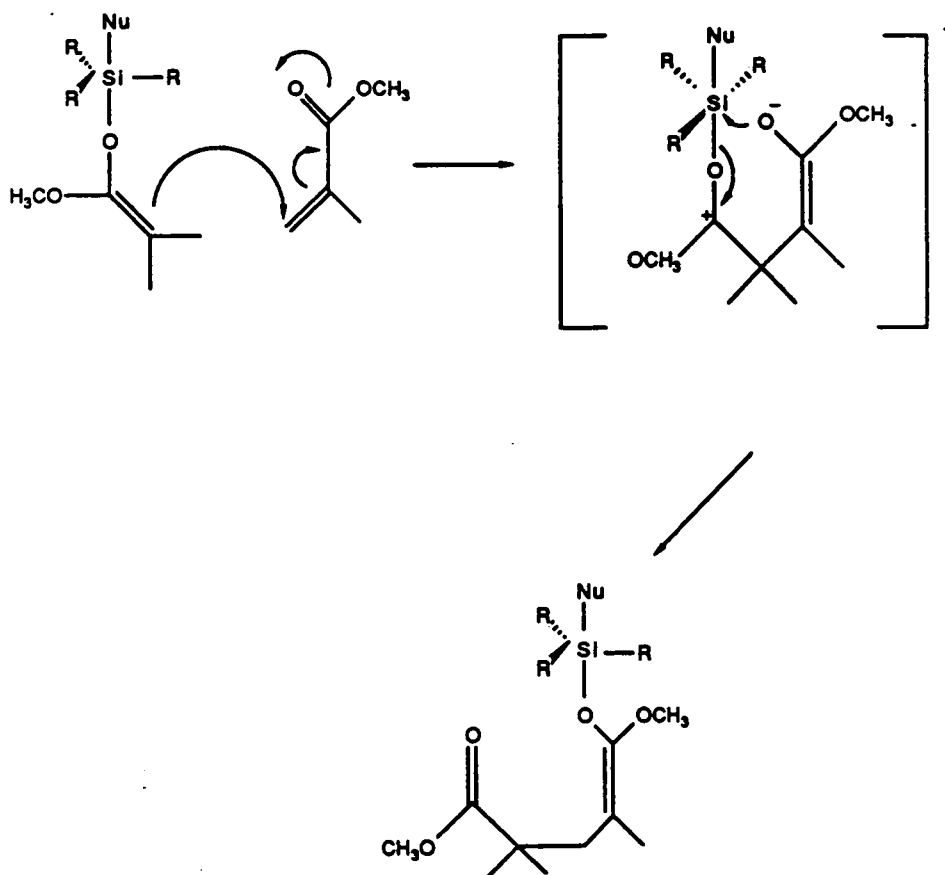
TABLE 11: COMPARISON OF THE ENERGY OF ACTIVATION VALUES FOR GTP AND ANIONIC MECHANISMS

	Ea (kJ/mol)	logA	kp
GTP(TASHF ₂)	16.9	6.8	56
Free Anion	---	---	2,100
Na ⁺ , 222	---	---	270
Cs ⁺	19.5	7.3	30
K ⁺	19.3	7.2	2
Na ⁺	18.3	7.0	34
Li ⁺	24.0	7.4	2

Ref.122. Mai, P.M.; Müller, A.H.E. Makromol. Chem., Rapid Commun. 1987, 8, 247-253.

followed by the transfer of the silyl group to the newly formed enolate (Scheme 14)[124]. Though one could anticipate the formation of a free enolate as the propagating center, this seems to be highly improbable based on the lower rate constants for GTP relative to those determined for anionic polymerization with free or cryptated anions and from the labelling studies of Farnham and Sogah which were previously addressed [115,116]. The proposed addition of monomer via a two step associative mechanism for GTP is very similar to anionic and radical mechanisms. Hence one would anticipate similarities in stereochemistry to be observed. The following section will address the question of microstructure.

MICROSTRUCTURE. The addition of monomer to the propagating chain end gives rise to the resulting microstructure in both anionic and GTP mechanisms. As addressed previously, the observed microstructure in the anionic polymerization method is readily influenced by the appropriate choice of initiator, solvent and temperature. This is particularly important in the preparation of polymers with specific chemical and mechanical properties. It has been reported that the stereochemistry of PMMA prepared by GTP is independent of solvent [79]. It is, however, influenced by the nature of the catalyst and polymerization temperature though not to the degree reported



122. Mai, P.M.; Müller, A.H.E. Makromol. Chem., Rapid Commun. 1987, 8, 247-253.

Scheme 14. Two Step "Associative" Mechanism for GTP

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for anionic polymerizations. For Lewis acid catalysts, the GTP of MMA was reported to give PMMA with a ratio of 2:1 syndiotactic triads to heterotactic triads regardless of solvent or temperature [93]. The anion catalyzed GTP of MMA at ambient temperature yields PMMA with nearly 1:1 syndiotactic to heterotactic composition. Performing isothermal polymerization studies with TASHF₂ and TASF, the precise determination of the effect of temperature on microstructure of PMMA in THF has been determined [77,126,127]. As the temperature of polymerization is decreased the syndioselectivity increases.

From the triad and diad composition information, more insight into the stereopolymerization mechanism was obtained [126]. It has been determined that the polymerization follows Bernoullian statistics, and hence, the configuration of the last monomer unit of the propagating chain end influences the addition of the next monomer unit. The triad information obtained compares well with the data obtained for the anionic polymerization of MMA with free anions or with cryptated sodium as the counterion. This conflicts with the concerted associative mechanism for GTP where high stereoselectivity would be assumed. It does however, provide favorable support for the two step associative mechanism where the primary role of the catalyst can be determined to activate the α carbon of the acetal to attack the polarized vinyl group of the monomer.

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Further studies into the stereopolymerization of monomers by GTP has involved the E/Z isomerization of the ketene silyl acetal initiator or chain end. Initial studies reported by Brittain [128], elucidated that the E/Z stereoisomerization of the chain end was competitive with propagation for TPSHF_2 as the selected catalyst, resulting in the observed Bernoullian statistics for the GTP of MMA. However, the E/Z stereoisomerization was slow for TBABB and one would predict non-Bernoullian statistics though this has not been the case observed. Brittain proposed the stereochemical behavior of Z and E chain ends to be similar and the favored mechanism of E/Z stereoisomerization to be a reversible Michael reaction giving rise to the Bernoullian propagation statistics.

OTHER CONSIDERATIONS. GTP has been described as a living polymerization mechanism, hence the molecular weight is determined by the ratio of monomer to initiator. It has been demonstrated that number average molecular weight can be easily controlled in the 1,000 and 20,000 gm/mole range, and with highly pure reagents, higher molecular weights can be achieved ($> 100,000$ gm/mole) [79]. As discussed in the free radical section, molecular weight can be controlled to some extent through the use of chain-transfer agents. Using chain transfer agents lower molecular weights can be obtained in GTP without the use of large quantities of the

LITERATURE REVIEW

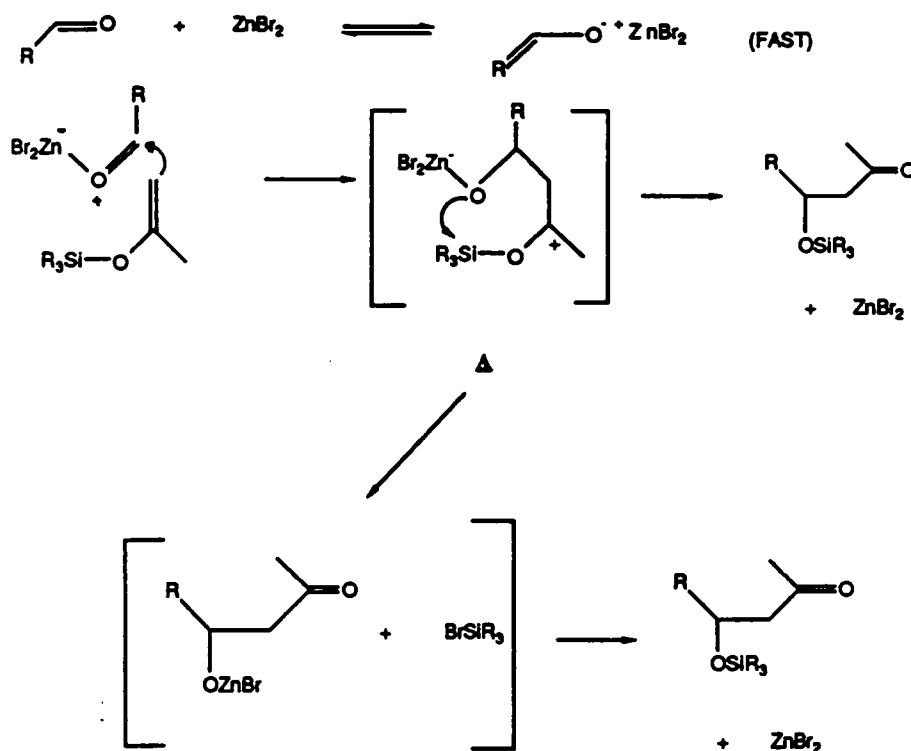
more costly ketene silyl acetals. Hertler et al., [129,130] has reported on the use of a variety of carbon acids as efficient chain transfer agents in GTP.

In accordance with the kinetic scheme for the associative mechanism, if the rate of initiation is equal to or faster than the rate of chain propagation the Poisson distribution that requires all the chains to grow at the same time may be obeyed. Thus, the molecular weight distribution or polydispersity is quite narrow. However, it has been documented that the polydispersity of polymers obtained by GTP may vary considerably depending on the mode of addition of reagents [124]. When the concentration of monomer is relatively low throughout polymerization; i.e. slow addition of monomer over time, molecular weight distributions as low as 1.05 have been cited. In contrast, when the concentration of monomer is high throughout polymerization; i.e. addition of catalyst to monomer and initiator solution, broader distributions (≥ 1.3) were obtained. From kinetic investigations using a batch addition of monomer, Müller, has also shown a nonlinear dependence of molecular weight vs conversion, though at complete conversion the experimental molecular weight usually agrees with the calculated value. The deviations from ideal living behavior have been attributed to the equilibration rates between activated and nonactivated chain ends which is proposed to be influenced by the concentration

of monomer at any given time [124,125]. Another likely possibility relates to impurities or side reactions.

Despite the deviation from living behavior reported, from kinetic investigations for the molecular weight dependence, it has been demonstrated that the GTP method affords near monodisperse living methacrylate polymers of well-controlled molecular weight [77]. In addition, duPont workers have taken advantage of organic synthetic methods and the general concept of GTP to polymerize monodisperse silyl vinyl ethers of controlled molecular weight [113,114,130,131]. In general, the initiator in the GTP process reacts with the monomer to regenerate the reactive functional group originally present in the initiator. The polymerization of silyl vinyl ethers, termed aldol-GTP, takes advantage of the known reactivity of aldehydes towards silyl vinyl ethers. It is proposed that addition of silyl vinyl ether to the initiator or propagating chain end takes place via transfer of the silyl group from monomer to initiator (Scheme 15). Many electrophiles have been used as initiators for this mechanism, but aromatic aldehydes are especially suitable. As in GTP, aldol-GTP proceeds in the presence of a catalyst, of which zinc halides were preferred. Investigations are in progress to elucidate the intermediates involved in this mechanism. However, from Scheme 15 some similarities to the GTP of acrylic monomers can be recognized. It is proposed that transfer of the

LITERATURE REVIEW



113. Sogah, D.Y.; Webster, O.W. In Recent Advances In Mechanistic and Synthetic Aspects of Polymerization; Fontanille, M., and Guyot, A., Eds.; NATO ASI Series 215; D. Reidel Publishing: Dordrecht, Holland. 1987; pp 61-72.

Scheme 15. Proposed Mechanism for Aldol-GTP

silyl group could occur through two possible intermediates. Transfer could occur in a concerted fashion; i.e., via a six-membered cyclic β -silyl stabilized carbocation (Scheme 15A), or as a two step process; i.e. formation of a Zn-alkoxide and silyl halide which react to form the desired product (Scheme 15B). Use of aldol GTP as a synthetic tool permits the polymerization of various silyl vinyl ethers to high conversion over a broad temperature range. In addition this living polymerization technique leads to the facile preparation of homo and block copolymers of a variety of architectures.

SUMMARY. Though the details of the mechanism of GTP and aldol-GTP have not been resolved entirely, these mechanisms have proven to be versatile in the living polymerization of selected families of monomers. Polymerization of monomers proceeds in a "living" manner with high chain end stability over a broad temperature range. The degree of control over molecular weight and molecular weight distribution rivals that afforded through living anionic polymerization methods for the preparation of alkyl methacrylates, and living cationic polymerization methods for silyl vinyl ethers. Both of these methods, GTP and aldol-GTP, have originated from organic synthetic methods and have been elegantly applied to the controlled synthesis of living polymers of a variety of architectures.

LITERATURE REVIEW

Though there has been a growing emphasis on new synthetic methods for the preparation of materials with controlled polymer parameters, the ability to prepare multicomponent systems with tailor-made properties is of considerable interest. The impact of multiphase polymeric systems has been enhanced by the preparation of well-defined copolymers. Through sequential addition methods, block copolymers from living polymerization methods provide one of the most effective means of controlling structure and chain growth related parameters of polymers. The concluding section of this literature review will briefly highlight the various methods of preparing well-defined multicomponent systems through chain growth polymerization techniques.

WELL-DEFINED MULTICOMPONENT POLYMER SYSTEMS

INTRODUCTION. Multicomponent or multiphase polymer systems have received a considerable amount of attention in recent years [65,133,134]. Multiphase materials are usually characterized by the presence of two or more polymeric phases in the solid state. These materials can be obtained in the form of blends, block and graft copolymers, composites or interpenetrating networks [10,63]. Though blends are more economical, most homopolymers are immiscible, and macrophase separation in the solid state,

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due to poor interfacial adhesion, leads to low strength materials. However, block and graft copolymers having sufficiently long sequences exhibit a tendency for microphase separation in the solid state. Microphase separation results in a highly dispersed multiphase morphology where the individual components are incompatible and as a result of intersegmental chemical linkages, the extent of phase separation between immiscible components is restricted. It is this microphase separated morphology which is responsible for some of the unique solution and solid state properties of these materials [63,133,135]. The unique properties, inherent to block and graft copolymers, are controlled to a large extent by their architecture. Variations in properties may be obtained by changing the chemical structure of the components, individual chain length, and/or the compositional ratio of the components with respect to each other [136-138]. The specific molecular architecture can be designed by using existing monomers or polymers. A brief overview to highlight the characteristics of some of the techniques to prepare well-defined block and graft copolymers via living polymerization methods will be presented. The reader is directed to the many review papers [65,137] and books [10,133] for a better appreciation of the vast number of polymeric systems that have been synthesized including, those achieved by step growth mechanisms.

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BLOCK COPOLYMERS. Since block copolymers, as well as graft copolymers, have found increasing commercial use as not only elastomers, but also as impact modifiers, adhesives etc., there has been a growing emphasis on new synthetic methods for their preparation [64,137]. Block copolymer structures are produced when extended sequences of one monomer are linked to extended sequences of another chemically dissimilar monomer. The sequential arrangement of these chemically dissimilar sequences allow for varying block repeating structures to be synthesized: AB diblock, ABA triblock, $[AB]_n$ multiblock or segmented repeating structures.

Numerous detailed reviews have been published on the subject of block and graft copolymers that describe the vast scope of techniques used to prepare these materials [65,133,137,139]. Though many synthetic methods have been employed, the sequential addition of monomers via living polymerization techniques is one of the most useful. In the absence of termination reactions, these sequential addition methods inherently allow for the synthesis of well-defined block copolymers of predictable molecular weight and block architecture. The spectrum of mechanisms that permit the formation of block copolymers via these sequential addition techniques include, anionic [41,139], cationic [140-142], GTP [68,77], iniferter [143,144] and even coordination

mechanisms [145]. In view of the "living" nature of these mechanisms the sequence length of the blocks are controlled by sequential or incremental addition of monomer. This general method of preparing block copolymers by sequential addition has been readily adapted to commercial production of a number of block copolymers, such as styrene-diene copolymers, (e.g. Kratons) and their hydrogenated derivatives [42].

Not only are block copolymers obtained by successive monomer addition, but multiblock copolymers, specifically triblocks, of low polydispersity or defined heterogeneity, can be prepared by either suitable coupling reactions or with difunctional initiators. Regardless of the method employed; sequential addition of monomers, difunctional initiators or coupling of living copolymers, living polymerization techniques for the preparation of block copolymers are limited by two basic factors [25]:

- I. the monomers involved must be polymerized to a high degree of conversion by the selected polymerization technique
- II. the propagating species generated by the first monomer must be capable of rapidly initiating the polymerization of the succeeding monomer.

In spite of these limitations, the high reactivity of living chain ends enables the preparation of chelic and telechelic polymers. The use of suitable capping reagents, as well as masked initiators, to prepare functional polymers

with reactive end groups could serve as building blocks for copolymers of predetermined architecture [64,139,146]. The interaction of functionally terminated oligomers is a versatile method for producing copolymers which is classically used in step-growth polymerization where the end groups are a natural consequence of the polymerization chemistry. Functionalization is of great interest since it provides an opportunity to modify the properties of polymers or block copolymers. Of particular interest are functionally terminated polymers; i.e. carboxyl or sulfonate, which lead to ionomer-type block copolymers [147-148]. The coupling of living polymers with monofunctional, difunctional or multifunctional reagents leads to the preparation of a variety of architectures; diblocks, triblocks, or star-block polymers. Although numerous functionalization reactions have been reported for living polymerization mechanisms, the chief difficulty in these functionalization reactions is quantitative transfer of the capping reagent to the propagating chain end. This is also a problem evident in the coupling of two living chain ends [149].



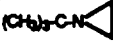
In addition to the preparation of these chelic and telechelic copolymers to bridge various polymerization methods, the late D.H. Richards et al. [150,151], proposed a general method which expands the array of monomers which can be copolymerized for the formation of multicomponent

systems. In general, this method, referred to as a transformation reaction, makes it possible to change the mode of polymerization from the mechanism of the first monomer to a mechanism best suited for the propagation of the second monomer. Three basic stages are involved in the transformation synthesis [152]:

- I. monomer A is polymerized by mechanism I and the propagating end is capped with a stable yet potentially reactive functional end group
- II. polymer A, is isolated, characterized, and dissolved in a solvent suitable for the polymerization of the second monomer B
- III. the functional end group of polymer A is transformed into a species capable of polymerizing monomer B by mechanism II

That is, the preformed polymer A is used as a macroinitiator for polymer B. Indirectly, one polymerization mechanism is transformed into another in order to incorporate into the copolymer combinations of blocks that cannot be prepared by a single mechanism. A number of block copolymers, covering a wide range of polymerization mechanisms, have been successfully prepared using transformation reactions (Table 12) [152-159]. A potential complication inherent to transformation reactions, which leads to the lower efficiency of controlled block formation, stems from unidentified impurities present in the macroinitiator system that may retard or inhibit the second polymerization mechanism. Another practical limitation is

Table 12. A Brief List of the Various Mechanisms Coupled in Transformation Reactions

1 st Mechanism	Initiating Functional group	2 nd Mechanism	Ref.
Cationic / Tetrahydrofuran	$\text{M-O}(\text{CH}_2)\text{C} \begin{array}{c} \text{Bu} \\ \\ \text{CH} \end{array} \text{Li}^+$ 	Anionic / Styrene	152
Anionic / Styrene	Poly(styrene)-Br $[\text{Mn}_2(\text{CO})_{10}]$	Free Radical / Alkyl Methacrylates & Acrylates	153
GTP / MMA	PMMA $[\text{Mn}_2(\text{CO})_{10}]$	Free Radical / Styrene	154
Condensation / $\text{HOOC}(\text{CH}_2)_4\text{OOH} +$	ClOC-R-COCl AgClO_4	Cationic / THF	155
Cationic / THF	$\sim\text{CO}(\text{CH}_2)_2\text{C}=\text{N}=\text{N}(\text{CH}_2)_2\text{CO}\sim$	Free Radical / Styrene or MMA	156
Free Radical / Styrene	isopropylxanthate terminated poly(styrene)	Free Radical / Styrene MMA or Methacrylic acid	157
Condensation Bisphenol A	macroazoinitiator	Free Radical / Styrene Various Alkyl Methacrylates	158
Anionic / Hexamethyl- cyclotrisiloxane	PDMS-Si(CH ₂) ₃ -O-SO ₂ -  -CH ₃	Ring Opening / Cyclic amines 	159

the potential macroinitiator itself. Any limitation on the efficiency of formation of the macroinitiator at the chain end of the first block potentially lowers the efficiency of the transformation reaction. As a consequence, residual homopolymer may be an inconvenience if pure block copolymer is required, but for many applications, like blend compatibilizers, this might not be a major disadvantage. It can be concluded that transformation reactions are an effective means of forming block copolymers with combinations of components that are not readily available via other methods.

Recently, attention has been directed to the coupling of polymers bearing mutually reactive end groups to prepare novel block copolymers [160-163]. This method, as the transformation method, has the advantage of combining blocks of quite different nature which may be derived from various polymerization mechanisms. Though this method is not restricted to the stringent purity levels required in either sequential addition or transformation methods, it is subject to kinetic and thermodynamic obstacles. The low concentration of reactive end groups impinges a kinetic restriction that is quite critical when high molecular weight polymers are employed. As stated earlier, most polymer pairs are immiscible, especially as molecular weight is increased and this produces a thermodynamic restriction. In order to circumvent these problems, a number of

number of investigations have been carried out using an interfacial technique [160,163]. Paulus et al. [160] describes the details of the interfacial coupling technique, and focuses on the effect of the end group on coupling efficiency for the preparation of poly(ethylene oxide)-b-poly(styrene).

The formation of multicomponent via two or more different mechanisms is not limited to the preparation of block copolymers, but as been successfully applied to the preparation of graft copolymers of well-defined architecture.

GRAFT COPOLYMERS. Graft copolymers, like block copolymers, may be comprised of two chemically dissimilar monomers. Though single phase morphology is possible in graft copolymers, two-phase morphology is much more commonly observed. The morphology observed is greatly dependent on the volume fraction of the graft and backbone. There is considerable latitude as to the chemical nature of the backbone, as well as the graft segments and the various techniques for joining them [137]. Regardless of the technique to prepare graft copolymers design of graft copolymers with controlled architecture has limited the tailoring of these materials to specific applications. Not only is the presence of homopolymer contamination a potential problem, but control of the number of grafts per

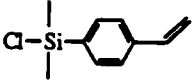
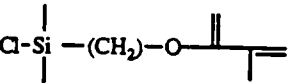
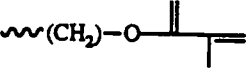
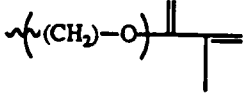
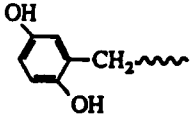
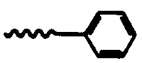
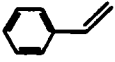
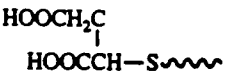
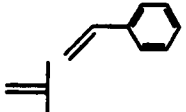

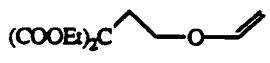
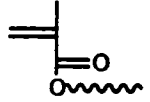
molecule, spacing of the grafts, and the number average length and polydispersity of each graft copolymer component is limited by some synthetic methods.

Relatively recently, better defined graft copolymer structures have been achieved through a technique which has been coined the Macromer^R method, an abbreviation for macromolecular monomer method or macromonomer method [164]. A number of reviews on this technique, first registered by R. Milkovich, have been published [36,165,166]. In general, Macromers^R are polymers having a polymerizable functional group at the chain end, which can be subsequently copolymerized with a comonomer. Table 13 [112,167-182] illustrates a variety of macromonomers that have been successfully copolymerized by a variety of mechanisms.

The general success of this method to incorporate macromonomers as branches in well-defined graft copolymers depends on two basic factors; the characteristics of the macromonomer, and its reactivity with a comonomer. The Macromer^R technique permits the characterization of the polymer prior to copolymerization [165,166]. Determination of the percentage of chain end functionality is important to reduce the amount of potential homopolymer contamination. The second factor, the copolymerization behavior of macromonomers, is at present not fully understood. A number of major factors influencing the reactivity have been recognized [166,173]. These include:

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Table 13. A Select List of Graft Copolymers Prepared Using the Macromer^R Method

POLYMERIZATION MECHANISM FOR MACROMONOMER / MACROMER	FUNCTIONAL GROUP	COPOLYMERIZATION MECHANISM / COMONOMER	REF.
Anionic / Poly(dimethyl-siloxane)		Free Radical / styrene	167
		Free Radical or Anionic / styrene, MMA	172
Anionic / Poly(styrene)		Free Radical / MMA	173
Condensation		Free Radical / Styrene	174
Anionic / Poly(styrene)		Condensation / poly(propylene)	175
Anionic / Poly(vinyl-pyridine)		Free Radical / styrene	176
Anionic / Polystyrene		Free Radical / MMA	177
Free Radical / PMMA		Condensation /	178
Cationic / Poly(2-phenyl 2-oxazoline)		Free Radical / styrene	179
Cationic / Poly(vinyl ether)			180
Cationic / polymers of isobutyl- & 2-benzoyloxyethyl vinyl ether			181
Anionic / Poly(styrene)		Group Transfer / MMA	112

- I. the reactivity ratio of the low molecular weight comonomer relative to the macromonomer to ensure random incorporation into the backbone
- II. kinetic excluded volume effects related to the diffusion controlled reaction of the polymerizable group relative to the molecular weight of the macromonomer
- III. thermodynamic repulsive interactions between unlike polymers, the macromonomer and propagating comonomer, giving rise to the non-homogeneous distribution of polymeric end groups

In spite of these influential parameters, a wide variety of macromonomers have been readily copolymerized with a broad number of comonomers by a diverse number of polymerization mechanisms (Table 13) [112,167-182]. An important feature over traditional methods of grafting, grafting to and grafting from the polymer backbone [181], is the strict control over molecular weight, polydispersity, and macromonomer structure when living polymerization methods are employed. As with other synthetic methods, the properties of graft copolymers synthesized using the macromer technique are dependent upon the individual chain length of graft and backbone, as well as the compositional ratio of the components with respect to one another. These attributes compound the difficulty to accurately characterize graft copolymers.

CHAPTER III**EXPERIMENTAL****PURIFICATION OF REAGENTS****SOLVENTS**

TETRAHYDROFURAN. Tetrahydrofuran (THF) (Fisher, Certified Grade) was refluxed under a nitrogen atmosphere in the presence of a sodium dispersion in paraffin wax. After complete dissolution of the paraffin wax with heat and stirring, a fine dispersion of sodium, having a higher surface area compared to sodium metal, remains to efficiently dry the solvent. Benzophenone was used as an indicator of solvent purity due to the formation of a highly colored dianion when reacted with sodium in the absence of protic sources and oxygen. After nearly one hour of refluxing, ca. 0.1- 0.3g of benzophenone (Aldrich) was charged to the THF/dispersed sodium mixture, and immediately one could see the deep purple color associated with the formation of the sodium/benzophenone ketyl. As an indicator benzophenone should be present in relatively small amounts.

It is also important to note, that an excess of sodium should be present to prevent the co-distillation of the benzophenone.

THF was refluxed in presence of the sodium/benzophenone ketyl under a nitrogen atmosphere for several hours prior to collection of the distillate for polymerization. Prior to collection of the THF fraction for polymerization, ca. 50-100 ml of distillate were removed as the first fraction. Subsequently, the polymerization fraction was collected into a clean, oven dried round bottom flask under a nitrogen atmosphere. Taking care not to expose the solvent to air and other impurities, the receiver flask was quickly fitted with a rubber septum, which was secured with copper wire, under a positive flow of nitrogen. The distilled THF was directly used in GTP of alkyl methacrylates by transfer of the solvent into clean dry reaction vessels. Despite rigorous purification of the solvent, it has been reported that anionic polymerizations indicate ca. 0.5-1.0 mmoles of impurities/1000 mls of purified THF [39].

CYCLOHEXANE. The major impurity present in most commercial grades of cyclohexane is cyclohexene [182], hence, cyclohexane (Fisher, Reagent grade) was stirred in the presence of concentrated sulfuric acid at room temperature for ca. two weeks in order to sulfonate the

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unsaturated impurities rendering them water soluble. The darkening of the sulfuric acid layer served as an indicator of the formation of sulfonated products from the olefinic impurities. The cyclohexane was then filtered through a column of basic alumina to remove acidic impurities into a low pressure (LP) holding tank for storage. Further purification involved fractional distillation in the presence of a sodium dispersion under a nitrogen atmosphere. In cases where extremely pure cyclohexane was needed, the above distillate was distilled from the living anion of sec-butyl lithium and 1,1 diphenylethylene.

ACETONITRILE. Acetonitrile is a very difficult solvent to dry because of its high affinity for water. Acetonitrile (Fisher, HPLC Grade) was dried over 4Å molecular sieves and distilled under a nitrogen atmosphere. After this preliminary drying it was subsequently dried over anhydrous calcium hydride and distilled [183].

CATALYSTS

Fluorides. Tris(dimethylamino)sulfonium difluorotrimethylsilicate ($\text{TASF}_2 \text{SiMe}_3$) (Aldrich) was recrystallized from a mixture of acetonitrile/THF (1/10 v/v). Tris(dimethylamino)sulfonium bifluoride (TASHF_2) was prepared in quantitative yield by the stoichiometric reaction of $\text{TASF}_2 \text{SiMe}_3$ with water in acetonitrile. The

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solvent and byproduct, hexamethyldisiloxane, were stripped under vacuum leaving the white powder $TASHF_2$. Purification was achieved by recrystallization from acetonitrile/THF (1/10, v/v) mixture [66]. The catalyst was dried under vacuum overnight. A solution of $TASHF_2$ in acetonitrile was prepared. Since the catalyst is very hygroscopic, a dry box was used. The catalyst was weighed and transferred to a volumetric flask in a dry atmosphere of nitrogen. Acetonitrile was charged to the flask. The molarity of the solution varied depending on the amount of catalyst that was charged.

ACETATES. Various tetra(alkyl)ammonium acetates were prepared from the dropwise addition of acetic acid to tetra(alkyl) ammonium hydroxide in water [184]. Acetic acid was added until the basic solution became neutral. The solvent was stripped to dryness and the solid residue was recrystallized from THF and dried under vacuum. Some of the tetra(alkyl) ammonium acetate salts could be purchased. Tetraethylammonium acetate (TEAA) (Aldrich) was recrystallized from acetone and dried under vacuum (200 millitorr). The acetate catalysts most frequently used in polymerization of MMA were tetramethylammonium acetate (TMMA) (Aldrich) and TEAA. Prior to polymerization dilute solutions of catalyst in THF were prepared. A stock solution of the selected acetate catalyst in purified THF

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was prepared and standardized via potentiometric titration with 0.0995 N alcoholic hydrochloric acid (Fisher) using a Fisher Titrator II.

BENZOATES. The tetrabutyl ammonium benzoate catalysts were prepared from purified benzoic acid (Aldrich) and aqueous tetrabutylammonium hydroxide [92]. To prepare tetrabutyl ammonium benzoate (TBAB) these reagents were mixed in a stoichiometric ratio in a separatory funnel. After the reaction subsided, the solution was extracted three times with 25ml aliquots of methylene chloride (CH_2Cl_2). The TBAB was extracted into the chlorinated solvent. At this point, if tetrabutyl ammonium bibenzoate (TBABB) was being prepared, an additional charge of benzoic acid (equivalent to the first charge) was added to the combined extracts. With the exception of this step the rest of the procedure was the same for either catalyst. The methylene chloride layer was dried with magnesium sulfate (MgSO_4), and filtered. The methylene chloride was removed by rotary evaporation, and the remaining solid was dissolved in warm THF. The volume was then reduced to ca. one half or until the catalyst began to crystallize. Dry ethyl ether was charged to the mixture for recrystallization. The crystals formed were washed with ether and dried under vacuum. In polymerizations where either TBAB or TBABB was the selected catalyst, 0.1g of the catalyst was dried ca. 16

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hrs under vacuum (0.5 torr) at 35 °C. Prior to polymerization, a 4M solution of TBAB or TBABB in THF was prepared.

MONOMERS

METHYL METHACRYLATE. Methyl methacrylate (MMA) (Rohm and Haas) was transferred to a clean, dried round bottom flask equipped with a Teflon^R stir bar. Finely divided calcium hydride was then charged to the flask and the flask was sealed with a rubber septum. The flask was purged with nitrogen until the evolution of hydrogen subsided. The monomer was stirred over calcium hydride for ca. 1-3 days. The monomer flask was fitted to a distillation apparatus and degassed during a cycle of freezing and thawing. Upon the final freezing cycle, the apparatus was flamed under vacuum. The monomer was vacuum transferred (ca. 200 millitorr) in a closed vacuum system to a receiver flask. In order to enhance the room temperature transfer, the receiving flask was cooled with a dry ice/isopropanol bath. After transfer, the monomer was transferred via a cannula under nitrogen into a sealed brown bottle, which had been previously flame dried under nitrogen and equipped with a septum. The bottle was pressurized and further sealed with Parafilm^R. The uninhibited monomer was stored at ca. -20 °C as a stock supply of MMA.

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Prior to polymerization, a clean distillation apparatus was flamed under vacuum to remove any moisture and oxygen. The cooled apparatus was filled with nitrogen and an aliquot of the calcium hydride pure monomer was transferred via a cannula to the apparatus. The monomer was thoroughly degassed using 2-3 freeze-thaw cycles. A 25 % (w/v) solution of triethyl aluminum (TEA) in hexane was employed to titrate the monomer for protic impurities. TEA was slowly syringed into the cold monomer until a yellow-green complex formed and persisted. A 25% excess of TEA was charged to the stable complex solution and the solution was allowed to stir in the absence of light at room temperature for ca. 30 min. The complexed solution was again degassed under a freeze-thaw cycle and the majority of the cyclohexane introduced from the titration with TEA was removed. The monomer was distilled under vacuum, frozen, covered with a black cloth, and used within 24 hrs of the distillation.

t-BUTYL METHACRYLATE. A calcium hydride dried stock of t-butyl methacrylate (TBMA) (Rohm Tech, W. Germany) was prepared in a similar manner to the procedures described for MMA. Prior to polymerization the cold, calcium hydride pure monomer was titrated with a mixture of diisobutyl aluminum hydride and TEA (10/90). This modification in the titration technique was incorporated to overcome the problem

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of the decreased reactivity of hindered alcohols with aluminum alkyls [39]. After titration, an excess of TEA was charged, and the solution was stirred in the absence of light for ca. 30 min. The monomer was distilled under vacuum as described for MMA though heat was required to assist the distillation of the higher boiling monomer.

2-ETHYLHEXYL METHACRYLATE. 2-Ethylhexyl methacrylate (EHMA) (Polysciences Inc.) stirred over calcium hydride was vacuum transferred as described for MMA. It was necessary to leave the valve open to the pump for constant vacuum and heat the flask (ca 70 °C) to transfer the monomer from the heterogeneous monomer solution due to the higher boiling point of the monomer. The distillate was stored and handled as described above for the other alkyl methacrylate monomers. The monomer was vacuum distilled prior to polymerization from the TEA/monomer complex. The contact time was increased for complete reaction of impurities with TEA relative to the time necessary for MMA. Typical contact times ranged from 45-90 min. After completion of the freeze-thaw cycles, the monomer was distilled under constant vacuum at ca. 70 °C.

HEXAMETHYLCYCLOTRISILOXANE. Hexamethyl-cyclotrisiloxane (D₃) (General Electric) was purified by vacuum sublimation from a heterogeneous calcium hydride

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mixture. Since the amount of D_3 in the final cyclohexane solution is determined by difference, individual components; distilling and receiving flasks, stir bar, calcium hydride and D_3 , were weighed prior to purification. The monomer was melted ($70\text{ }^\circ\text{C}$) and stirred over finely divided calcium hydride (ca. 16 hrs). After complete sublimation, enough purified cyclohexane was transferred via a cannula into the receiving flask to dissolve the sublimed crystals. The solution was then transferred under nitrogen via a cannula into a clean 1000 ml volumetric flask equipped with a septum. The solution was diluted with cyclohexane. The molarity of the solution was determined using the weight of D_3 determined by difference. The solution was transferred to a clean dry brown bottle and served as a stock solution for polymerizations.

INITIATORS

METHYL TRIMETHYLSILYL DIMETHYL KETENE ACETAL. The purity of methyl trimethylsilyl dimethyl ketene acetal (MTS) (Aldrich) was checked using gas chromatography (GC) and proton NMR. The purity was ca. 90-95% by GC analysis depending on the lot of MTS used. Other contaminants were c-silylated product from the synthesis of initiator as well as the decomposition product, methyl propionate. MTS was purified by distillation at $45\text{ }^\circ\text{C}/15\text{ mm Hg}$ using a model 800 micro spinning band distillation apparatus (B/R instrument

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Corp). The purity of the distillate was determined by GC to be ca. 98-99%. Purification of MTS, at the same temperature and pressure, with a microdistillation apparatus achieved the same level of purity when the temperature and pressure were carefully controlled.

For some model studies, MTS was also prepared via a hydrosilylation reaction [76]. Various levels of catalyst and temperatures were employed during the study, hence a calculated amount of tris(triphenylphosphine)chlororhodium I (Wilkinson's catalyst) was charged to a dry reaction vessel. The flask was sealed with a septum and pressurized with 6-8 psi of nitrogen. An aliquot of MMA was charged followed by the addition of either trimethylsilane or dimethylethylsilane. Trimethylsilane is a gas at room temperature, hence transfer was accomplished by passing the gas into a cold, sealed graduated cylinder. The appropriate amount of silane was then transferred as a liquid into the cooled reaction vessel of MMA and catalyst. When dimethylethylsilane was employed the aliquot needed was transferred using a syringe. With either silane, the hydrosilylation was permitted to proceed at various temperatures during the study.

**2-(TRIMETHYLSILOXY)ETHYL (DIMETHYLETHYLSILYL)
DIMETHYLKETENE ACETAL.** 2-(Trimethylsiloxy)ethyl
(dimethylethylsilyl) dimethylketene acetal (OH-MTS) was

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prepared from purified 2-hydroxyethyl methacrylate (HEMA). Silylation of the hydroxyl functional group proceeded through the addition of trimethylchlorosilane to 2-hydroxyethyl methacrylate. The reaction was carried out in tetrahydrofuran (THF) at 0 °C. Neutral reaction conditions were maintained by the presence of triethylamine acting as the acid acceptor [94]. The triethylamine hydrochloride salts were removed through filtration and the 2-(trimethylsiloxy)ethyl methacrylate was distilled prior to hydrosilylation. 0.1 mole % (based on methacrylate) of Wilkinson's catalyst was charged to a dry reaction vessel and the flask was subsequently pressurized with 6-8 psi of nitrogen. The protected methacrylate was charged to the flask followed by the slow addition of dimethylethylsilane. The hydrosilylation reaction proceeded for ca. 16 hrs. at 50 °C under a nitrogen atmosphere affording a silyl ketene acetal hydroxyl functional initiator [76]. The initiator was vacuum distilled prior to use (47 °C/15mm Hg). Both silylation of the hydroxyl functional group and hydrosilylation forming the ketene silyl acetal were monitored using ^1H NMR and FTIR.

t-BUTYL(DIMETHYLETHYLSILYL)DIMETHYLKETENE ACETAL.

t-Butyl(dimethylethylsilyl)dimethylketene acetal (t-Butyl MTS), which would permit the preparation of an acid functionalized polymer via GTP, was synthesized from t-butyl

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methacrylate via a hydrosilylation reaction using Wilkinson's catalyst. The procedure for the hydrosilylation is similar to that described above for OH-MTS. The product was vacuum distilled prior to use (45 °C/ 12mm Hg).

sec-BUTYLLITHIUM. sec-Butyllithium (Lithco Division of FMC) was obtained as ca. 1.4 M solution in cyclohexane. In order to reduce the extent of contamination from insertion of syringes, small aliquots of the solution were transferred to sealed, pressurized serum bottles. The molarity was then determined by titration using 2,5-dimethoxybenzyl alcohol, a self indicating standard [185]. The solutions were stored at ca. -20 °C. sec-Butyllithium not only served as an initiator for the anionic ring opening polymerization of D₃, but also as an indicator of reactor purity in the kinetic experiments.

TERMINATING REAGENTS

3-METHACRYLOXYPROPYLDIMETHYLCHLOROSILANE. 3-methacryloxypropyldimethylchlorosilane (Petrach) was used in most cases as received since an excess (2-5 mole%) of silane was charged to ensure quantitative functionalization. In situations where an excess of terminating agent was not permissible, the reagent was vacuum distilled (ca. 200 millitorr, 45 °C and characterized by proton NMR.

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At times the availability of the reagent was limited, hence synthesis of the material was accomplished via hydrosilylation in the presence of chloroplatinic acid. Allyl methacrylate was charged to a sealed reaction vessel which was previously pressurized with a nitrogen atmosphere. Chloroplatinic acid, 0.001 mole % relative to allyl methacrylate, was charged and finally, purified trimethylchlorosilane was slowly added. The exotherm of reaction was carefully monitored to prevent polymerization of the allyl methacrylate and decomposition of the catalyst. The terminating agent was isolated by distillation and characterized using proton NMR.

OTHER REAGENTS

SODIUM. Sodium (Aldrich) was obtained as a dispersed metal in paraffin wax and used as received.

BENZOPHENONE. Benzophenone (Aldrich) was used as received. In combination with sodium it served as an indicator of solvent purity for THF.

4Å MOLECULAR SIEVES, ALUMINA AND SILICA (Fisher). These drying agents were dried at 110 °C in a vacuum oven for ca. 24-48 hrs and used immediately after activation. The

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primary purpose of these reagents was for solvent drying or removal of inhibitors from monomers.

TETRA(ALKYL)AMMONIUM HYDROXIDE. The various alkyl ammonium hydroxides (Aldrich) were obtained either in aqueous or methanolic solutions and were used as received. These were primary reagents used for the preparation of GTP acetate and benzoate catalysts.

BENZOIC ACID. Benzoic acid (Aldrich) was recrystallized twice from toluene and dried under vacuum. A melting point of 123 °C was obtained for the product.

TRIETHYLALUMINUM. Triethyl aluminum (TEA) (Ethyl Corporation) was obtained as 25 weight % solutions in hexane and used without further purification. For ease of handling due to their pyrophoric nature and to avoid excessive contamination from syringe insertions, the solutions were carefully transferred into sealed, pressurized serum bottles. The solutions were then stored at room temperature in a flame retardent cabinet.

DIISOBUTYLALUMINUMHYDRIDE. Diisobutylaluminum-hydride (Ethyl Corporation) was obtained as a 25 weight %

solution in hexane. This material was handled and stored as described for TEA.

TRIS (TRIPHENYLPHOSPHINE) CHLORORHODIUM (I). This catalyst known as Wilkinson's catalyst (Aldrich, gold label) was used as received in the preparation of the ketene trialkylsilyl acetal initiators. Hydrosilylations in the presence of this catalyst yield a high (~95%) percentage of the 1,4 addition product [72,73].

CHLOROPLATINIC ACID. Chloroplatinic acid (Aldrich) was used as received for the hydrosilylation reaction of allyl methacrylate and vinylbenzyl chloride [167,168,172]. Temperature during the reaction was controlled to prevent the decomposition of the catalyst.

TRIALKYLSILANES AND TRIALKYLCHLOROSILANES (Petrach). Due to the hydrolytic instability of these silanes and chlorosilanes, distillation of the material under nitrogen atmosphere was carried out prior to use in the various hydrosilylation [72,] and protecting group reactions [97]. In situations where trimethylsilane was employed, the gas was used as received.

TRIETHYLAMINE. Triethylamine (Aldrich) was distilled prior to use (35°C). It was used as an acid acceptor.

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ALLYL METHACRYLATE AND 2-HYDROXYETHYL METHACRYLATE. Allyl methacrylate and 2-hydroxyethyl methacrylate (Aldrich) were dried over 4Å molecular sieves and vacuum distilled. These materials were not used as monomers in GTP, but as reagents for preparing either functional initiators or terminating agents.

TITRANTS. 2,5-dimethoxybenzyl alcohol (Aldrich) and 0.9995 N hydrochloric acid (Fisher) were used as received for the titration of various reagents. sec-Butyllithium solution in hexane was titrated with 2,5-dimethoxybenzyl alcohol. This is a convenient self indicating standard for the determination of organolithium reagents [185]. When solutions of sec-butyllithium / cyclohexane in THF are treated with the titrant, the initial reaction produces the colorless solution of the alkoxide. When deprotonation of the hydroxyl group is complete the organolithium reagents react to form a mixture of intensely colored red dianions. The development of this color at the endpoint is practically instantaneous and requires less than 0.01 mmole. equiv. excess of organolithium reagent to be visible. This method does not account for the presence of alkoxides in the system as does the Gilman "double titration" [186]. The 0.9995 N HCl was standardized and used in the potentiometric titration of various tetraalkyl ammonium acetates in THF.

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1,1 DIPHENYLETHYLENE. 1,1-Diphenylethylene (Kodak) was purified via vacuum transfer. sec-Butyllithium was used to titrate the crude reagent. The formation of the red anion, 1,1 diphenylhexyllithium (DPHL) served as indicator. The reagent was then vacuum transferred from the complex (ca. 200 millitorr). DPHL is a common anionic initiator, its primary function in this research was to serve as a conditioning agent for the low pressure reactor.

POLYMER SYNTHESIS

POLY(ALKYL METHACRYLATE) HOMOPOLYMERS. With the exception of the kinetic investigations, the GTP of all alkyl methacrylate monomers were carried out in round bottom flasks. The flasks and stir bars were cleaned and dried in a convection oven (110 °C) for a minimum of 24 hrs. prior to use. Immediately prior to use they were quickly removed from the oven and sealed with a rubber septum. The flasks were flamed and allowed to cool while purging with nitrogen. Though the nitrogen was prepurified, dryness was further insured by passing the gas through a column (3' x 2") containing activated molecular sieves. A clean dry thermocouple was typically inserted to monitor the exotherm of polymerization.

The polymerization solvent, THF, was transferred to the polymerization vessel using either a syringe or cannula.

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The amount of solvent charged was based on the weight percent solids and final molecular weight desired. In the homopolymerization investigations, 10-20 weight percent solutions were typically used. The relative amounts of initiator and monomer were determined as shown in equation. 10 and 11

$$g(\text{monomer}) / (g/ml) (\text{monomer}) = ml(\text{monomer}) \quad \text{Eq. 10}$$

$$g(\text{monomer}) / (g/mole)_{\text{polymer}} = \text{moles}_{(\text{in})} \quad \text{Eq. 11}$$

$$[\text{moles}_{(\text{in})} \times (g/mole)_{(\text{in})}] / (g/ml)_{(\text{in})} = ml_{(\text{in})}$$

$$\text{moles}_{(\text{in})} / \text{ratio } \#(\text{variable}) = \text{mole}_{(\text{cat})} \quad \text{Eq. 12}$$

$$[\text{mole}_{(\text{cat})} \times (g/mole)_{(\text{cat})}] / [g(\text{cat})/ml(\text{THF})] = ml_{\text{solution}}(\text{cat}/\text{THF})$$

polymer = theoretical polymer molecular weight
 in = initiator
 cat = catalyst

The GTP catalysts used throughout these investigations were all nucleophiles, hence the amount of catalyst required for polymerization was determined relative to initiator (Equation 12). The selected catalyst was in a stock solution of an appropriate solvent. The calculated aliquot was used for polymerization.

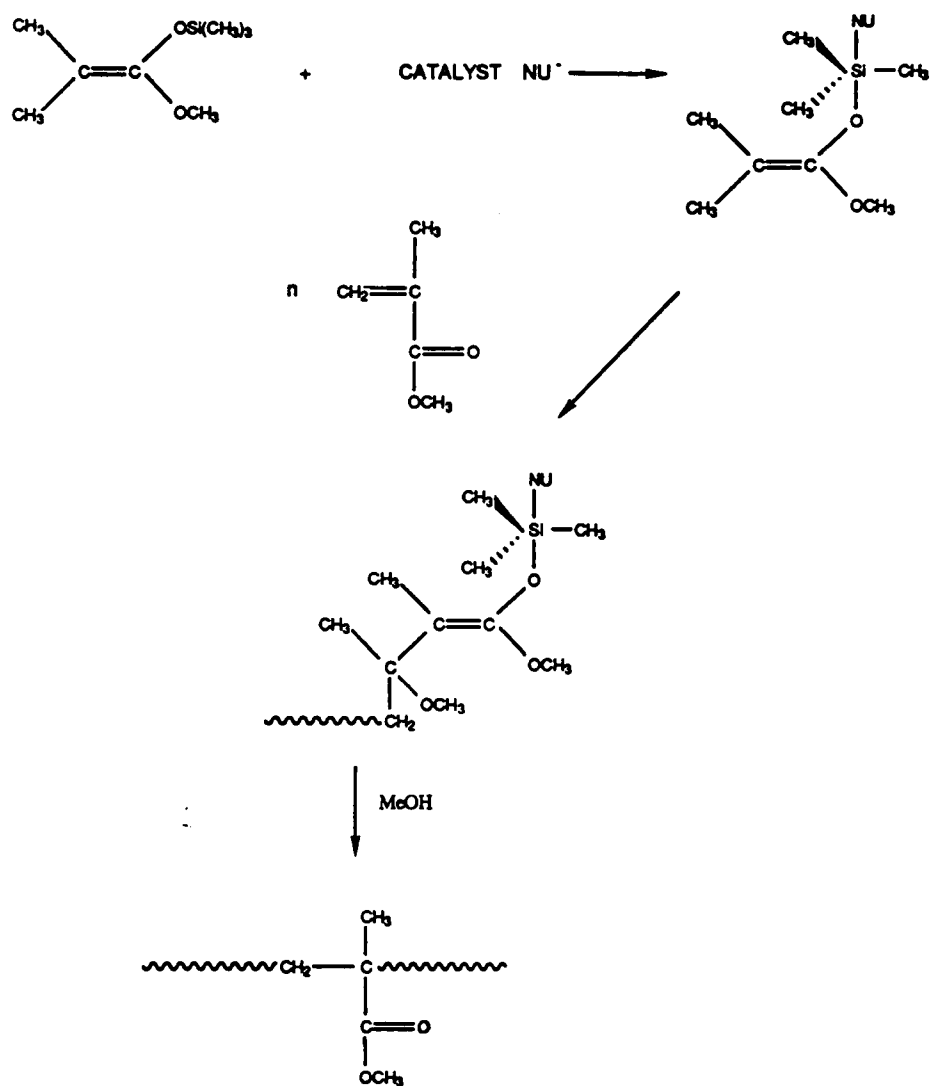
EXPERIMENTAL

The GTP reactions were usually conducted at room temperature, except when temperature dependent studies were carried out. Scheme 16 illustrates the order of addition of reagents. The initiator and catalyst solution were first charged to the polymerization vessel and allowed to complex, forming the proposed pentacoordinate intermediate. The time for complexation varied depending on the strength of the nucleophile.

The trialkyl aluminum purified methacrylate was slowly added to the initiator/catalyst complex solution in order to control the exotherm of polymerization. Though slow addition of monomer was employed, reaction exotherms ranging from 5-20 °C were typically observed. The polymerizations were terminated after the exotherm of polymerization subsided (ca. 1hr.) with 0.2-0.5 mls of degassed, HPLC grade methanol. The homopolymers were precipitated in an appropriate nonsolvent (10x % excess). If protected initiators were employed in the GTP such as OH-MTS, deprotection was carried out in situ. Deprotection of OH-MTS using dilute acid yields hydroxyl functional polymer.

POLYMERIZATION OF MMA IN A "LIVING" POLYMERIZATION REACTOR. For kinetic investigations of the GTP of MMA, a low pressure reactor was employed (Figure 6). The reactor vessel was a commercially available unit consisting of a heavy-walled, flint glass bowl, a stainless steel top plate,

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Scheme 16. Order of Addition of Reagents For the GTP of MMA

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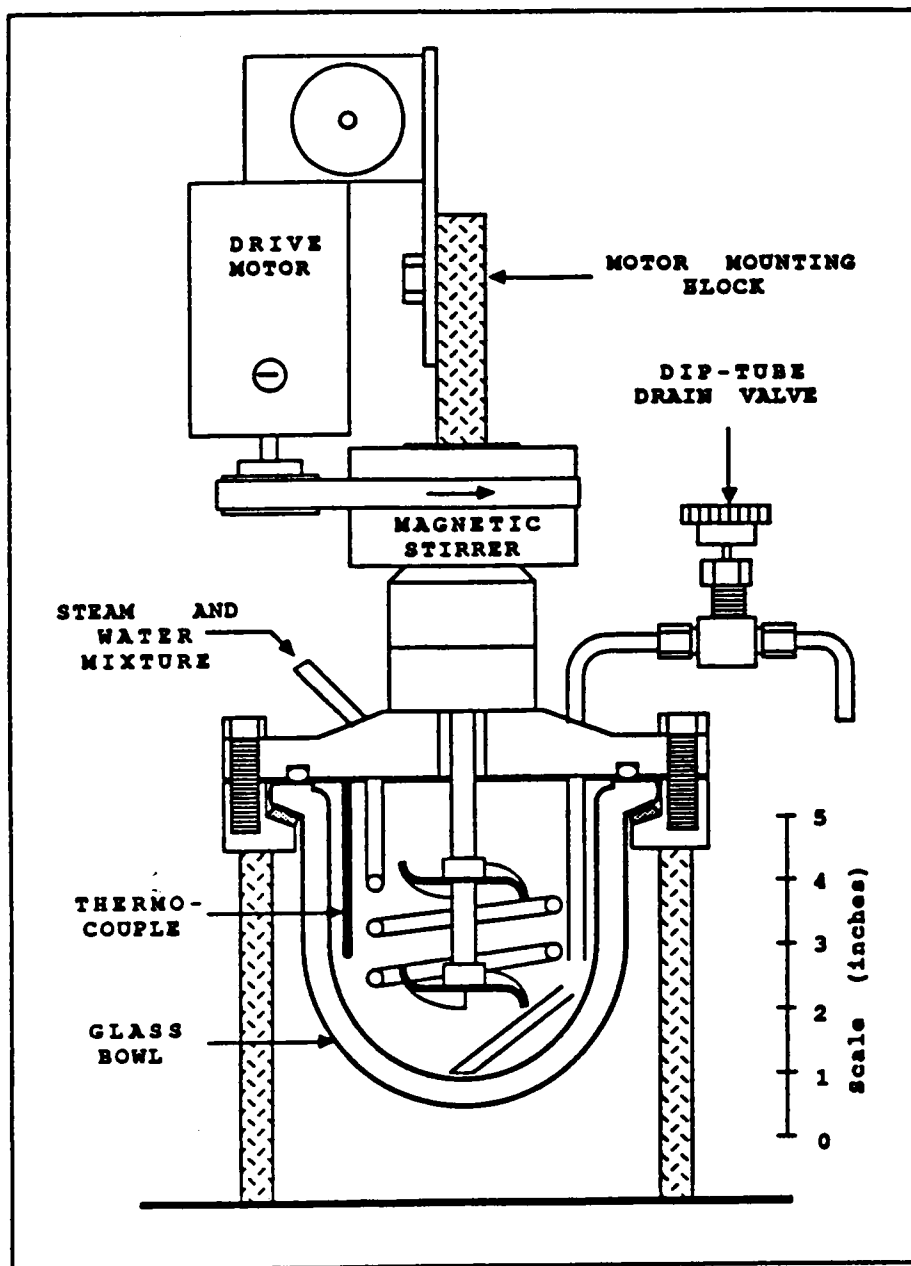


Figure 6. Diagram of the Low Pressure Polymerization Reactor

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as well as a magnetically coupled stirring assembly [187]. The top plate was equipped with septa ports for the addition of reagents via syringe and a dip tube for the removal of samples and solvents. The reactor was equipped with coils through which a steam water mixture flows for precise control of reaction temperature. The temperature control for the reactor was provided by a system consisting of a single solenoid valve, and a relay-equipped thermistor type controller. The controller opens (or closes) the solenoid valve when the reactor temperature exceeds (or lags) the set point by 0.1 °C, thus relatively constant temperature control was provided. A more detailed description of the assembly and utility of this reactor can be found in reference 187.

Prior to polymerization the reactor was conditioned to insure the removal of protic impurities. The conditioning involved the following procedure: Cyclohexane (ca. 500 ml) was cannulated into the nitrogen pressurized reactor and heated to 60 °C with stirring. A 2 mmole charge of 1,1-diphenylethylene was added to the solvent. The solution was titrated with sec-butyllithium (1.4 M in cyclohexane). Upon titration of the protic impurities a yellow color formed indicating the formation of diphenylhexyl lithium anion (DPHL). To this complex a 2 mmole charge of sec-butyllithium was added and allowed to react with 1,1-diphenylethylene. The deep red color of the DPHL anion

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persists and indicates that the reactor system is free of protic impurities and leaks. After the conditioning, the anion solution was drained and the vessel was filled and rinsed twice under nitrogen with cyclohexane, followed by a THF rinse before the solvent for the polymerization was introduced.

After the rinsing cycle, 450 ml of THF was transferred into the reactor for the polymerization study. The reactor temperature was set and allowed to reach equilibrium prior to addition of other reagents. The mode of addition of reagents began with the charge of initiator, MTS, followed by the addition of an aliquot of the tetrabutylammonium benzoate (TBAB) solution. The TBAB charge was based on the moles of ketene silyl acetal. The initiator and catalyst were allowed to complex for ten minutes. Trialkyl aluminum purified MMA was quickly charged via a syringe to the reactor and this point was defined as time zero ($t=0$). Samples were removed with time into septa sealed vials containing degassed, HPLC grade methanol under a nitrogen atmosphere to quench the reaction. An aliquot of each sample was removed for proton NMR analysis. The remaining unreacted monomer and solvent was removed by rotary evaporatio and dried to constant weight under vacuum. The polymers were analyzed by gel permeation chromatography.

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POLY(ALKYL METHACRYLATE)-b-POLY(ALKYL METHACRYLATE) COPOLYMERS. All methacrylic block copolymers were prepared using GTP via sequential addition techniques and coupling reactions. Regardless of technique the first block was prepared according to the procedures outlined for homopolymer preparation via GTP. A sample of the first block was quenched in degassed methanol for characterization. After complete conversion of the first monomer, the second purified monomer was charged via syringe to the propagating ketene trialkylsilyl acetal. Again the polymerization was permitted to proceed until complete conversion of the second monomer. In the preparation of diblocks, the polymerizations were quenched with methanol. However in the preparation of triblocks, a sample of the second block is removed for analysis and another aliquot of the first monomer was charged to the living chain end. After sufficient time to ensure complete conversion, the polymerization was quenched and the block copolymer was isolated by precipitation in an 80/20 mixture of methanol/water.

To prepare copolymers by coupling living GTP chain ends, α, α' dibromoxylene was utilized. The polymerization vessel was submerged in an ice bath to lower the temperature to ca. 0 °C. α, α' Dibromoxylene was introduced in a solution of purified THF. The amount of coupling agent was

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equivalent to 1/2 the moles of initiator theoretically calculated.

POLY(DIMETHYLSILOXANE) HOMOPOLYMERS. The anionic ring opening polymerizations of hexamethylcyclotrisiloxane (D₃) were carried out in rigorously cleaned and dried one-neck round bottom flasks. Each flask was equipped with a magnetic stir bar and sealed with a rubber septum. The flasks were flamed while purging with nitrogen. D₃ in cyclohexane was charged to the cooled reaction vessel via syringe. The polymerization was initiated at room temperature with a solution of sec-butyllithium in cyclohexane. The charge of initiator was determined from equation 13.

$$\text{mole}(\text{initiator}) = \frac{g(\text{monomer})}{(\text{g/mole})_{\text{polymer}} \text{ calculated MW}} \quad \text{Eq. 13}$$

After ca. 1 hr. to insure efficient initiation, a ca. 10 percent by volume charge of purified THF was introduced to the reaction vessel to promote propagation of the living silanolate species. After 48 hrs, 3-methacryloxypropyl dimethylchlorosilane was charged to terminate the polymerization. Termination with the chlorosilane derivative of allyl methacrylate afforded a methacrylate end group. A stoichiometric amount of terminating agent relative to living chain ends was employed in most

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instances. A 5-10% excess of the terminating agent was used to insure efficient capping only when the polymer was precipitated in methanol. Isolation of the polymer was also accomplished via filtration using a dried column of celite to prevent the introduction of protic impurities, such as residual methanol. The column of celite and the receiving flask were flamed under a nitrogen purge. The polymer was transferred via a cannula to the sealed column and passed through the column under nitrogen pressure to remove the lithium chloride salts, byproduct of the termination step. The solvent, cyclohexane was removed by stripping under vacuum, and the isolated polymer was dried further in a vacuum oven.

POLY(DIMETHYLSILOXANE) MACROINITIATOR. Methacrylate functional PDMS was charged to a dried one-neck round bottom flask which was degassed under vacuum (500 millitorr) for 1-2 hrs. The vessel was pressurized to 6-8 psi with dry nitrogen. A 0.1 mole% charge of Wilkinson's catalyst based on moles of methacrylate end groups was added. Subsequently, a 20 mole% excess (based on methacrylate end groups) of dimethylethylsilane was charged via syringe. The hydrosilylation reaction proceeded for ca. 24 hrs. at 50 °C under a nitrogen atmosphere affording a ketene trialkylsilyl acetal.

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POLY(METHYL METHACRYLATE)-b-POLY(DIMETHYLSILOXANE) COPOLYMERS. Copolymer preparation proceeded using the macroinitiator prepared as described above. The flask containing the GTP macroinitiator, the ketene trialkyl silyl acetal functional PDMS, was stripped under vacuum (150 millitorr) to remove any residual ethyldimethylsilane. After pressurizing the vessel with nitrogen (6-8 psi), purified THF was charged to the reaction vessel via syringe to afford ca. 10 weight percent solution. An aliquot of tetrabutylammonium benzoate catalyst solution in THF was charged to the flask. The TBAB charge was based on the theoretical moles of ketene trialkyl acetal functionality on the PDMS. Macroinitiator and catalyst complexed and after 5 min. triethyl aluminum purified MMA was slowly charged. Sizable exotherms were not typically observed during block copolymer formation, hence reactions were usually terminated 1-2 hrs after initiation. The reactions were terminated with degassed methanol and precipitated in methanol. The dried block copolymers were extensively extracted with hexanes to remove any residual PDMS homopolymer.

POLY(METHYL METHACRYLATE)-g-POLY(DIMETHYLSILOXANE) COPOLYMERS. The GTP copolymerizations of the PDMS macromer with MMA were carried out in rigorously cleaned and dried one-neck round bottom flasks equipped with a magnetic stirrer. A calculated amount of PDMS macromonomer was

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charged to the reaction flask prior to sealing it with a rubber septum. The macromonomer was thoroughly degassed in the reaction vessel, followed by the pressurization of the flask with 6-8 psig of nitrogen. A sufficient concentration of THF (the polymerization solvent) was charged to yield solutions of ca. 10 percent (w/v) MMA. The order of addition of reagents was modified relative to the preparation of alkyl methacrylate homopolymers. MMA was charged to the reaction vessel. The addition of a calculated amount of initiator, MTS, followed. An aliquot of the catalyst concentration was quickly charged. The reactions were terminated by addition of 0.2-0.5 ml of degassed, HPLC grade methanol. The polymers were precipitated in methanol and dried in a vacuum oven. Residual, unincorporated PDMS homopolymer was removed by extensive extraction of the copolymer with hexanes in a Soxhlet extractor. The copolymers were dried under vacuum prior to characterization.

STRUCTURAL ANALYSIS

Fourier Transform Infrared Spectroscopy (FTIR) is a rapid, direct and nondestructive method for obtaining qualitative and quantitative information. FTIR was performed on a Nicolet MX-1 spectrometer (resolution = 4.0

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cm^{-1}). Samples were typically scanned from 4000 cm^{-1} to 600 cm^{-1} and individual regions were expanded for closer examination. Results were reported in the absorbance mode. Only small amounts of sample were required and the mounting of the sample in the spectrometer was dependent on the sample.

Polymer Analysis. In the case of poly (alkyl methacrylate), samples were usually cast onto salt plates from tetrahydrofuran or methylene chloride solutions. In some instances free standing films were used by suspending the film in front of the laser source. Polymer analysis was usually performed due to the ease and speed of the technique in examining various functional groups.

Initiator Analysis. FTIR provided a facile means to follow the formation of initiators prepared from various alkyl methacrylates as well as methacrylate terminated poly(dimethylsiloxane) (PDMS) oligomers. Samples were placed between two salt plates using a syringe to minimize exposure to moisture. In situations where functional groups on the ester carbonyl were present, FTIR provided a simple method for observing the protection of these groups prior to the hydrosilylation reaction. The analysis of the hydrosilylation product verified the conversion of the ester carbonyl (1723 cm^{-1}) with the formation of a C-O-S bond

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indicative of the ketene silyl acetal (1705 cm^{-1}). This technique, in conjunction with proton NMR, permitted definition of the appropriate reaction temperature for the hydrosilylation of alkyl methacrylates to silyl ketene acetals. This was particularly important to establish the quantitative conversion conditions for the preparation of the PDMS macroinitiator. Due to the extreme hydrolytic instability of the C-O-Si bond an absorption at 1732 cm^{-1} indicating the hydrolysis of the ketene silyl acetal was always evident.

Nuclear Magnetic Resonance. NMR was a versatile tool for the analysis of a wide variety of compounds prepared during the course of this research.

a) Proton NMR. ^1H NMR was performed on a Bruker WP 270 instrument and spectra were obtained in CDCl_3 solutions (3-5% wt/vol). In some instances CDCl_3 was acidic enough to cause hydrolysis of the reagent; hence, the lock solvent, CDCl_3 , was sealed in a capillary tube and placed inside the 5mm NMR tube. Proton NMR was used extensively to examine the purity of reagents such as initiators and catalysts. ^1H NMR, in conjunction with FTIR, provided a convenient way to examine the formation of initiators with time. In particular, macroinitiator formation was followed over time with ^1H NMR using either a Bruker WP 270 or IBM NR 80 (Appendix 1).

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High resolution NMR was also used for the structural and stereochemical analysis of polymers. ^1H NMR was used to monitor the course of polymerization during kinetic investigations. Integration of the vinyl protons with respect to the α -methyl protons, indicative of the polymer stereochemistry, permitted the determination of the extent of conversion at various times for the polymerization of MMA using tetrabutylammonium benzoate as the selected catalyst. For poly(methyl methacrylate) ^1H NMR adequately provided the elucidation of stereochemical information. The various tactic conformations of the methyl protons were resolved allowing for the determination of the % tacticity by simple integration. Overlapping resonances for other alkyl methacrylates resulted in poorer resolution hence ^{13}C NMR was used for the analysis.

Proton NMR provided a method for determining the structure of the end group. This was particularly useful for the characterization of PDMS oligomers. The functionality of these oligomers could not be quantitatively determined by this technique, but was easily determined using ^{29}Si NMR. For low molecular weight samples (< 3000 g/mol) the integral of the resonance associated with the chain end was ratioed with respect to the integral of a resonance that occurred in each repeat unit.

Further utility of ^1H NMR was evident in the determination of copolymer composition for various block and

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graft copolymers. Compositional determination was achieved by the ratio of the integration of a resonance associated with one monomer unit to the integration of a resonance associated with the comonomer. For example, the composition of a poly(methyl methacrylate)-g-poly(dimethylsiloxane) copolymer was determined by the ratio of the methyl ester resonance at 3.5 ppm to the silicon methyl resonance at 0.1 ppm. The compositional determination of all methacrylic block copolymers was restricted due to resolution limitations, hence; ^{13}C NMR was employed.

Silicon 29 NMR. Silicon 29 NMR is a useful tool for the determination of chain end functionality since the chemical shift of the silicon resonance is readily affected by small changes in the nature of the substituents [188]. Methacrylate functionality was confirmed by ^{29}Si NMR (Bruker WP 200 spectrometer). For quantitative measurements, an inversegated pulse program was employed to decouple the protons and eliminate the nuclear Overhauser effect (NOE). A relaxation agent, 0.4 M chromium(III)acetylacetonate ($\text{Cr}(\text{acac})_3$) solution in CDCl_3 was employed to shorten the relaxation time (T_1) as well as to help suppress the NOE [189]. Other functionalized PDMS oligomers were analyzed to confirm assignments. Integration of the silicon atom adjacent to the initiating fragment with respect to the integration of the resonance resulting from the silicon atom

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adjacent to terminating group gave rise to the percent functionality of the oligomer. In a similar manner, integration of the silicon atom adjacent to the initiating fragment with respect to the integration of the resonance resulting from backbone silicon atoms provided an alternate route to the determination of molecular weight. Silicon 29 NMR was also used to determine the efficiency of the hydrosilylation reaction forming the ketene silyl acetal PDMS macroinitiator.

Carbon 13 NMR. Using a Bruker WP 200 SY spectrometer, high resolution 50 MHz ^{13}C NMR spectra of polymers were obtained. Polymer solutions (15% wt/vol) were prepared in CDCl_3 . As in silicon 29 NMR, a relaxation agent $\text{Cr}(\text{acac})_3$ (0.4M) was employed in combination with an inversegated proton decoupling program. ^{13}C NMR was conveniently used for the determination of stereochemistry of various poly(alkyl methacrylates) as well as copolymer composition for all-methacrylic copolymers.

SEPARATIONS

Gas Chromatography (GC) (Varian Vista 6000). The sensitivity of ^1H NMR was found to be limited in the determination GTP initiator purity. GC was routinely used to determine the purity of initiator after vacuum distillation. Neat samples of each fraction were injected

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onto a 30 meter methylsilicone capillary column and analyzed using a method which can be found in Appendix 2.

Supercritical Fluid Fractionation. Poly(methyl methacrylate)-g-poly(dimethylsiloxane) copolymers were fractionated using supercritical fluid extraction (SCFE) as a method to determine the chemical composition distribution. The SCFE procedures were performed at Phasex Corporation. The extractions were carried out isothermally at 120 °C using chlorodifluoromethane (CDFM) above its critical temperature ($T_c = 96$ °C) and pressure ($P_c = 716$ psia). The copolymers were fractionated using an increasing pressure profile from 1500 psig to 4000 psig in an apparatus illustrated in Figure 7. Individual fractions were collected at ambient pressure in glass u-tubes after the pressure letdown valve. Sample sizes of ca. 10 grams were separated into fractions of sufficient size for characterization by NMR and GPC.

MOLECULAR WEIGHT DETERMINATION

Ultraviolet-Visible Spectroscopy (UV). UV spectra were obtained from a Perkin Elmer 552 instrument scanning from 350nm to 190nm at 20nm/min. 214nm was established as the wavelength maximum for the unsaturated methacrylate group of the PDMS oligomers. MMA in cyclohexane was used as the

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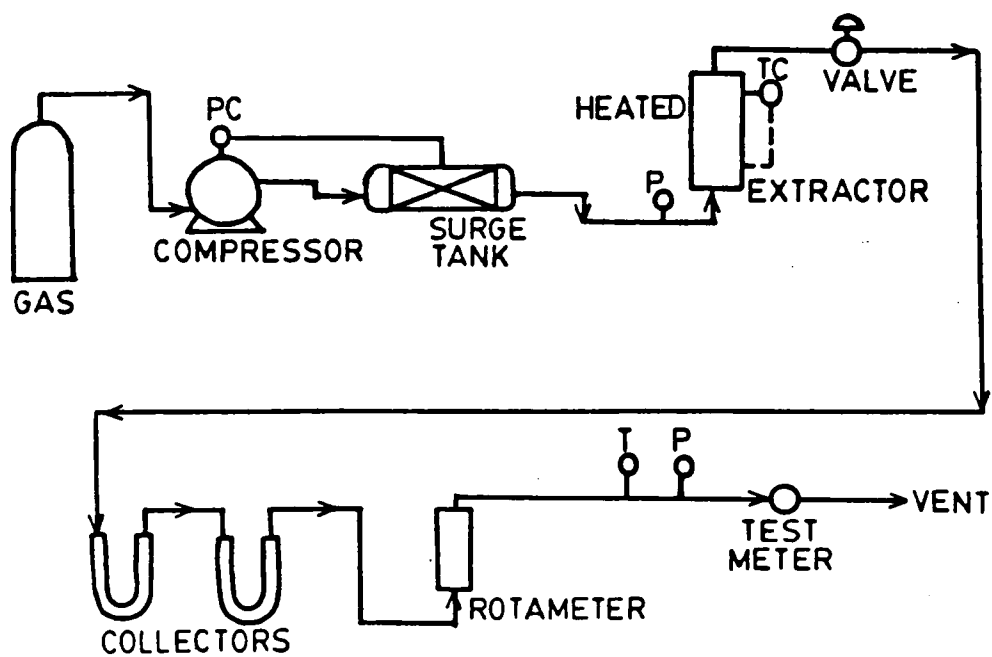


Figure 7. Supercritical Fluid Extraction Apparatus

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standard to prepare a Beer-Lambert Law plot. From this plot the extinction coefficient was determined to be 6863 l/mol. Macromonomer solutions of known concentration were prepared in cyclohexane. The absorbance was read from the UV instrument for at least 5 different concentrations of each sample. The absorbance was then extrapolated back on the Beers Law plot to a methyl methacrylate concentration. Dividing the macromonomer concentration (g/L) by the methyl methacrylate concentration (mol/L) the functional molecular weight was obtained (Equations 14 and 15).

$$C_{MMA} = A / \epsilon b \quad \text{Eq. 14}$$

$$\langle Mn \rangle = C_{\text{macromer}}(\text{g/L}) / C_{MMA}(\text{mol/L}) \quad \text{Eq. 15}$$

Vapor Phase Osmometry. Vapor phase osmometry was carried out in toluene at 80 °C using a multistandard technique for calibration. In order to prepare a calibration curve standards of varying known molecular weight were evaluated. These are:

Standard	MW(g/mol)
Squalene	410
Sucrose Octaacetate	678
Polystyrene	1800
Poly(methyl methacrylate)	7800
Poly(methyl methacrylate)	13000
Poly(methyl methacrylate)	19700

For each standard, four concentrations were prepared in toluene. At least four voltage readings were taken for each

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concentration. A plot of the average voltage change (ΔV) vs concentration yields the slope ($\Delta V/C$). Plotting $1/M_n$ vs $\Delta V/C$ yields the calibration curve to be used for the VPO measurements of various polymers (Equation 16 and 17).

$$\Delta V = C (\Delta V/C) + b \quad \text{Eq. 16}$$

$$1/\langle M_n \rangle = (\Delta V/C) m + b' \quad \text{Eq. 17}$$

Similarly, four concentrations of each polymer to be analyzed were prepared in toluene. For each concentration at least four voltage readings were taken. A plot of the ΔV vs concentration was prepared. Using the slope and intercept information from the calibration curve the number average molecular weight was determined by equations .

$$\Delta V = C (\Delta V/C) + b'' \quad \text{Eq. 18}$$

$$\langle 1/M_n \rangle = (\Delta V/C) m + b' \quad \text{Eq. 19}$$

where m = slope of the calibration curve
 x = slope of V vs C plot for polymer
 b' = intercept of calibration curve

Size Exclusion Chromatography. The molecular weight and molecular weight distributions were analyzed by Gel permeation Chromatography (GPC). The GPC (Waters 150-C17 GPC) was equipped with Ultra Styragel columns of 500, 10^3 , 10^4 , 10^5 , 10^6 Å porosity in THF. Typically polymers were analyzed using a UV detector set at 218nm. The number average molecular weights for poly(alkyl methacrylate)

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homopolymers and their various copolymers were based on PMMA standards. For the poly(dimethylsiloxane) oligomers, PDMS standards were used in the analysis of molecular weight and molecular weight distribution [190,191]. Though the presence of the methacrylate end group is sufficient to permit the analysis of molecular weight in THF using a UV detector, PDMS oligomers were also characterized by GPC using a column set in toluene using a refractive index detector. The porosities of these columns were 100, 500 and 1000 Å. Again, PDMS standards were used for the molecular weight and molecular weight distribution determination. In all cases a program was used to analyze the GPC data by both linear and cubic fit [36].

THERMAL ANALYSIS

Differential Scanning Calorimetry (DSC). DSC thermograms were obtained with a Perkin Elmer DSC-2 using a heating rate of 10 °C/ min. Glass transition temperatures were measured at the midpoint of the transition. Samples were either powders or solvent cast films.

Dynamic Mechanical Thermal Analysis (DMTA). DMTA spectra were obtained on a Polymer Labs DMTA at a frequency of 1 Hz. Using a scan rate of 5 °C/min. a temperature range

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spanning -150 °C to 150 °C was examined. Samples used were typically compression molded films.

Thermal Gravimetric Analysis (TGA). TGA data was obtained on a Perkin Elmer System 2 instrument. Samples were analyzed under both nitrogen and air atmospheres at a heating rate of 10 °C/min. The samples were solvent cast from THF.

SURFACE ANALYSIS

Water Contact Angle Measurements. Advancing angle measurements were obtained using a goniometer. Firstly, homopolymer and copolymer samples were cast from dilute solutions onto metal ferro-type plates. The solvent, methylene chloride, was permitted to evaporate slowly. Using a goniometer, drops of water in increments of 2 microliters were applied to the surface of the polymer film until a total drop size of 20 microliters was obtained. Typically the angle increases until the drop size reaches ca. 6-8 microliters and then the measured angle levels off. The advancing contact angle measurements were averaged from three drop measurements per film. The variation in measurements across the film were approximately plus or minus one degree.

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X-Ray Photon Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA). XPS analysis was carried out on a Kratos XSAM-800 instrument with Mg anode, 200 watts at a vacuum of 10^{-9} torr. Films of the various samples were prepared as described for advancing contact angle measurements. Angular dependent XPS depth profiling was carried out to determine the surface composition of various PMMA-g-PDMS copolymers prepared by GTP as a function of surface penetration.

CHAPTER IV**RESULTS AND DISCUSSION****POLYMERIZATION OF ALKYL METHACRYLATES VIA GTP**

INTRODUCTION. As highlighted in the literature review, α,β unsaturated esters, more specifically alkyl methacrylates, have traditionally been prepared by anionic and free radical polymerization techniques. These were also the primary techniques utilized in our laboratories prior to 1984 for the polymerization of homopolymers as well as copolymers having an alkyl methacrylate component. With the presentation of GTP by duPont workers, we were also prompted to examine this technique for the polymerization of alkyl methacrylates. Initial investigations were concerned with developing the techniques to prepare various molecular

weight polymers of alkyl methacrylates and to demonstrate the degree of control over the polymerization methodology prior to ensuing the preparation of multicomponent systems, in which GTP is one of the mechanisms of polymerization.

CONTROLLED POLYMERIZATION OF ALKYL METHACRYLATES.

Under ideal conditions, there are no termination steps in living polymerization mechanisms, thus high purity conditions are required to obtain polymers of controlled molecular weights having Poisson molecular weight distributions. As in the anionic mechanism, GTP is susceptible to termination by the presence of trace amounts of protic impurities. In the presence of reactive protic impurities, the trimethylsilyl group is cleaved from the initiator, or propagating chain end, thus resulting in the termination of the living polymerization. Although the purity of reagents is a critical aspect of living polymerizations, it is not always appreciated. Initial investigations were centered around meeting the purity requirements of reagents; solvent, monomers, initiators and catalysts, for the controlled polymerization of alkyl methacrylates by GTP.

The purification of all reagents is described in detail in Chapter 3 and the purification of solvent, THF, and alkyl methacrylate monomers are the same as used to obtain high purity reagents for the anionic polymerization of alkyl

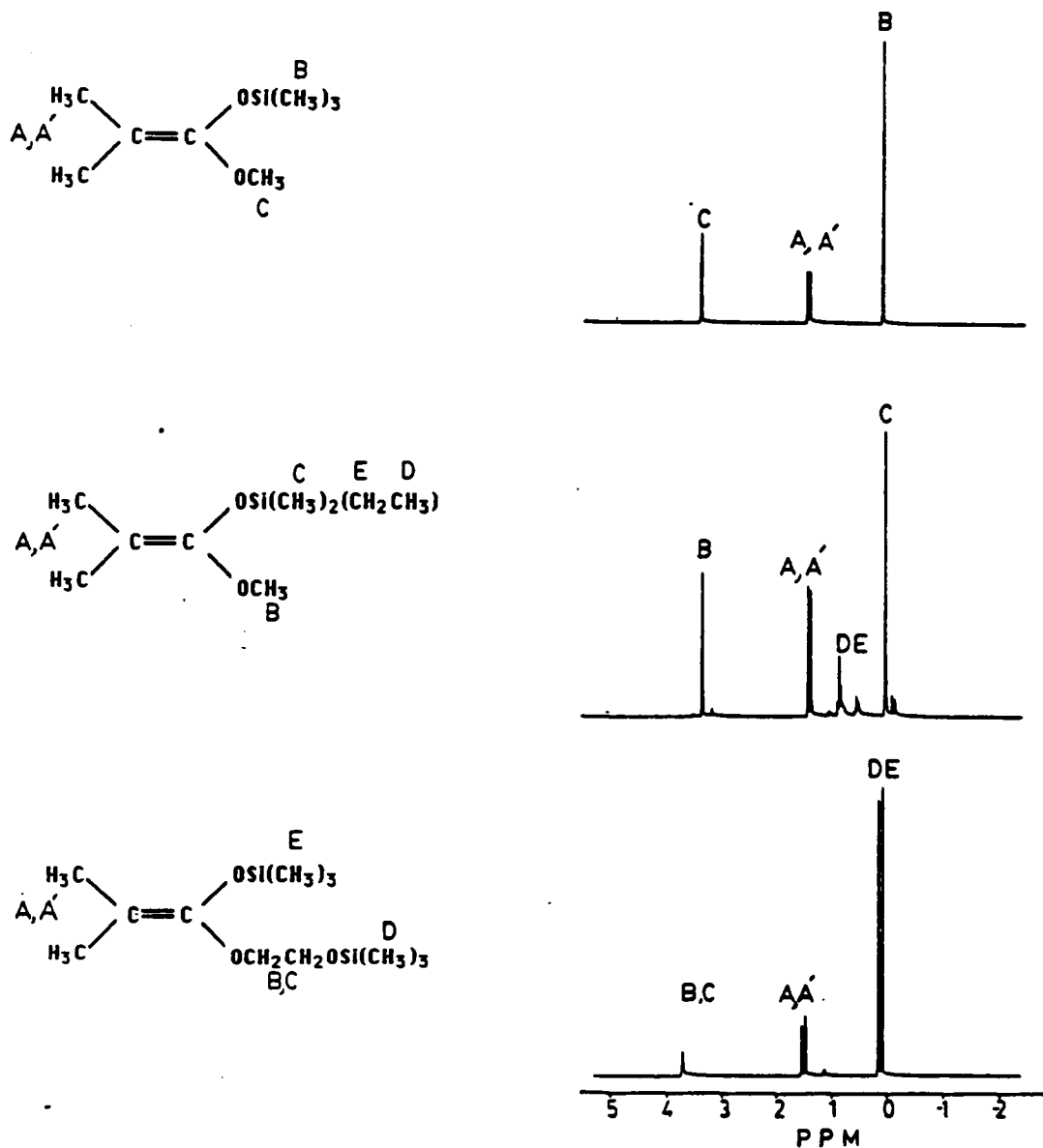
RESULTS AND DISCUSSION

methacrylates [47-48]. The use of trialkylaluminums as purification reagents to obtain ultra-pure alkyl methacrylate monomers was thoroughly studied by Allen and Long et al. [47-48] and briefly reviewed in Chapter 2 of this text.

Anionic polymerization of alkyl methacrylates using 1,1 diphenylhexyllithium (DPHL) as the initiator at -78°C allows for the titration of impurities present in the solvent and 1,1 diphenylethylene prior to the charge of organo-lithium. This results in knowing the exact concentration of the initial active concentration of initiator without the complication of impurities. The rate of formation of the red anion of DPHL is a function of the solvent nature, purity, and temperature. In GTP, titration of trace reactive impurities present in solvent, initiator and catalyst is not possible prior to monomer addition. Thus, using syringe techniques and relying on the purification of reagents, a methodology to prepare alkyl methacrylate polymers by GTP was established.

Initiators utilized throughout this work are shown in Table 14 with their ^1H NMR spectra. The most frequently utilized initiator during the initial investigations was dimethyl(methyltrimethylsilyl)ketene acetal (MTS). Purification of each initiator involved vacuum distillation

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Table 14. GTP Initiators and Their ^1H NMR Spectra

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and analysis of the distillate by GC using the method presented in Appendix 1 (Figure 8)

Unlike anionic and free radical polymerization mechanisms, GTP is catalyzed. It is this point that makes the fundamental study of this system more difficult in some respects than typical ionic polymerized systems, and this point will be brought out during the discussion of the kinetic investigations. A variety of nucleophilic catalysts were used throughout these investigations (Table 15). It has been proposed that the role of catalyst in the polymerization mechanism changes depending on its nature [82]. These characteristics have been reviewed in detail in the literature review.

In our initial studies using GTP for alkyl methacrylates, it was noted that the relative mole ratio of initiator to catalyst affected the molecular weight control and molecular weight distribution (Table 16). The effect of the level of catalyst will be more evident and discussed in more detail when the kinetic investigations are addressed.

This anomaly was also reported by Bandermann et al., [85] who utilized trimethylsilyl cyanide and $\text{TASF}_2\text{SiME}_3$ to systematically study the role of the catalyst in GTP. Unlike Bandermann's experimental efforts, acetonitrile was not utilized as the polymerization solvent in our studies, though a small amount was used to prepare a solution of TASHF_2 catalyst in THF/ CH_3CN to allow addition of the

RESULTS AND DISCUSSION

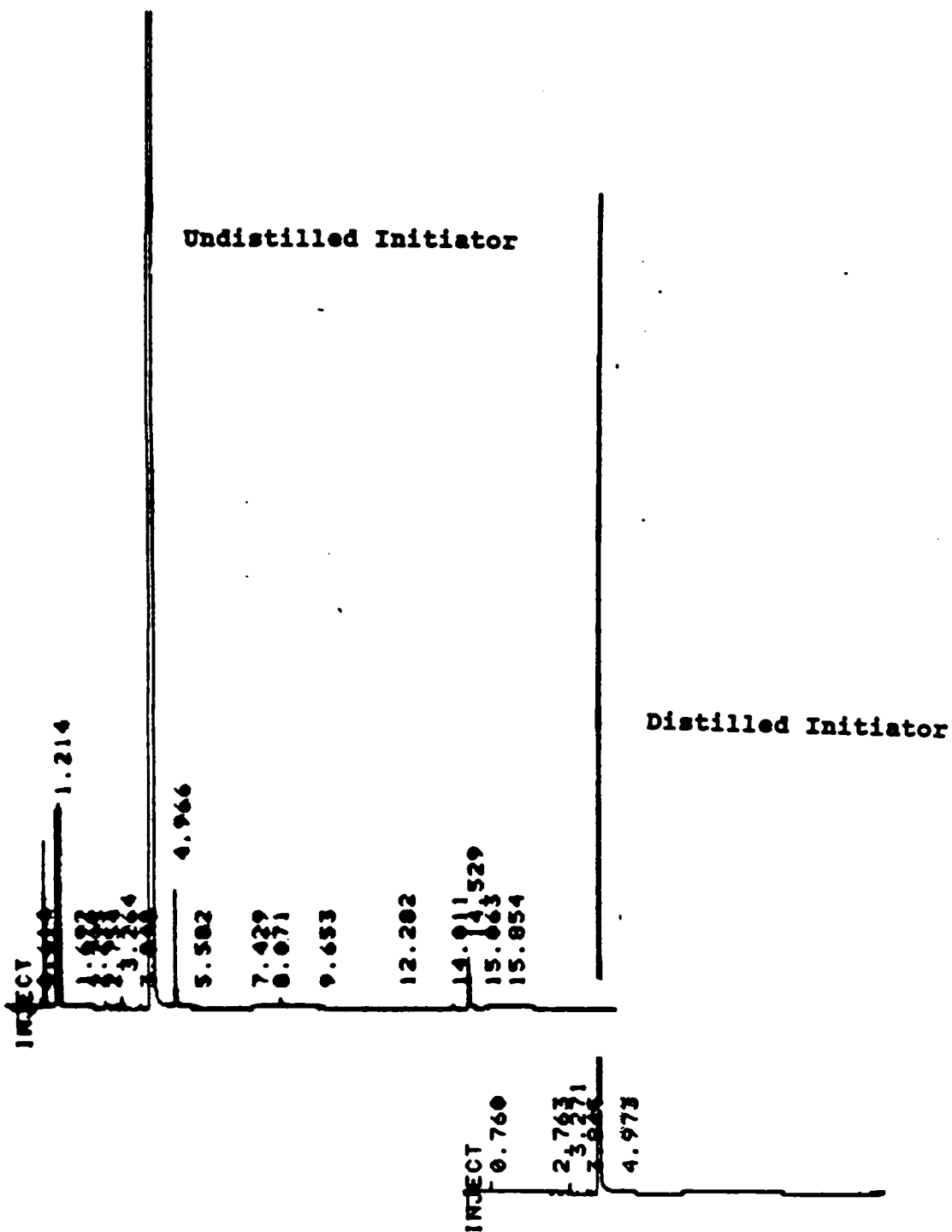


Figure 8. GC of purified MTS

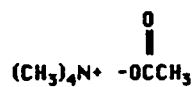
RESULTS AND DISCUSSION

Table 15. Catalyst Structures

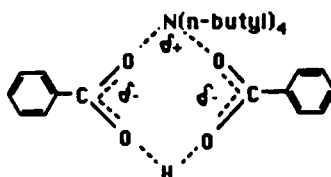
NUCLEOPHILIC CATALYSTS FOR GTP

TRIS(DIMETHYLAMINO)SULFONIUM BIFLUORIDE (TASHF₂)

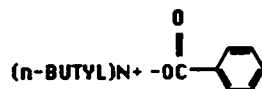
(TETRAMETHYL)AMMONIUM ACETATE (TMMA)



(TETRABUTYL)AMMONIUM BENZOATE/ BENZOIC ACID (TBAB/BA)



(TETRABUTYL)AMMONIUM BENZOATE (TBAB)



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TABLE 16: EFFECT OF CATALYST CONCENTRATION
ON MOLECULAR WEIGHT CONTROL^a

Initiator/catalyst ^b (mole ratio)	GPC ^c	
	<Mn>	<Mw>/<Mn>
3.4/1	81,800	1.46
5.0/1	77,500	1.29
7.5/1	44,200	1.19
15.0/1	33,900	1.15
50.0/1	21,300	1.13

^a Monomer = methylmethacrylate
Catalyst = TASHF₂
Solvent = THF

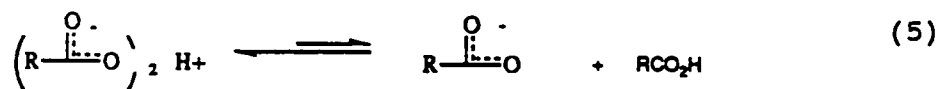
^b Catalyst concentration based on a
mole ratio to initiator concentration

^c Calculated MW = 25,000; <Mn> based on PMMA stds. in THF

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catalyst to the reaction vessel as a solution. In 1988 Sitz et al., [120] reported the identification of side reaction products that resulted in GTP due to the presence of acetonitrile. Prior to that investigation, though controlled GTP of MMA was possible with TASHF₂, our investigations drifted from using TASHF₂ as the catalyst for GTP to other species which did not require the presence of acetonitrile. Tetramethylammonium acetate showed limited solubility in THF and thus, it was often difficult to accurately report the concentration of catalyst utilized.

With the report of Dicker et al., [92] on the preparation of benzoate catalysts, our attention turned to the use of these catalysts primarily due to their ease of preparation and solubility in THF. One could directly prepare the monobenzoate species and bibenzoate from tetrabutylammonium benzoate and benzoic acid. Though no evidence for the actual structure of the bibenzoate exists, Dicker et al., [92] proposed that the bianions may serve as a pool providing mono-anions (5). This was supported by the lower concentrations of catalyst required vs the mono-benzoate.



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An alternative explanation for the requirement of lower concentrations of catalyst may be the enhanced nucleophilicity or basicity of the bi-benzoate over the mono-benzoate. It seems likely that the bibenzoate may form a structure similar to that of the bifluoride. In the bifluoride structure the proton is held between the two fluorine atoms [192], and is thus, incapable of interfering with polymerization as a reactive protic impurity. One would suspect, if the bibenzoate served as a pool for monoanions then the benzoic acid present in the system may prematurely terminate the polymerization. Doping of benzoic acid into a GTP polymerization using a catalyst incapable of complexing with it may resolve this question.

Table 17 illustrates the successful preparation of PMMA by GTP over a wide molecular weight range using a variety of catalysts. Continuing investigations have solely involved the use of tetrabutylammonium benzoate (TBAB) though the table reflects control of the polymerization methodology with each catalyst. It must also be noted that a mole ratio of initiator to catalyst was selected to maintain molecular weight control and a narrow polydispersity. This ratio varied depending on the catalyst used.

GTP OF VARIOUS MONOMERS. The GTP of MMA in the previous section has demonstrated to some extent the significant role of the catalyst in this polymerization

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TABLE 17: MOLECULAR WEIGHT CONTROL FOR THE GTP OF MMA WITH VARIOUS CATALYSTS

MW(calculated)	<Mn> (GPC) ^a	<MW>/<Mn>	Catalyst ^b
5,000	6,200	1.10	TASHF ₂
10,000	12,800	1.07	"
20,000	26,500	1.12	"
20,000	16,300	1.24	TMAA
100,000	101,900	1.29	"
25,000	26,700	1.09	TBAB/BA
50,000	64,000	1.12	"
1,000	2,000	1.17	TBAB
25,000	26,700	1.09	"
80,000	89,700	1.14	"

^a Based on PMMA stds. in THF

^b Catalysts Abbreviations

1. TASHF₂ = Tris(dimethylammonio)sulfonium bifluoride
2. TMAA = Tetramethylammonium acetate
3. TBAB/BA = Tetrabutylammonium bibenzoate
4. TBAB = Tetrabutylammonium benzoate

mechanism. Yet, it is the initiator, terminating agent and choice of monomer(s) that permit the design of materials with specific properties. The diverse number of reagents which have been utilized in GTP to prepare homo- and copolymers of various architectures were outlined in Chapter 2. We have employed a limited number of these in synthetic aspects involving GTP.

Having demonstrated the ability to prepare PMMA of various molecular weights via GTP, other monomers were homo- and copolymerized to show the extended utility of this technique (Table 18A). All of these monomers were polymerized using TBAB as the selected catalyst. It was noted that the exotherm of polymerization for the homopolymerization of t-butyl methacrylate was relatively insignificant relative to that observed for the GTP of MMA. Table 19 reports the tacticity information of these polymers in comparison to PMMA prepared using GTP. Unlike the ^1H NMR spectra of PMMA, resonance overlap prohibits the use of ^1H NMR to elucidate the tactic compositions for PTBMA and P2EHMA, hence, ^{13}C NMR was employed. It was difficult to determine the tactic compositions of poly(t-butyl methacrylate) based on the integration due to poor resolution. In addition the values reported for poly(2-ethylhexyl methacrylate) may not reflect the composition obtained under controlled temperature conditions since the polymerization temperature was not strictly monitored.

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TABLE 18: VARIOUS POLY(ALKYL METHACRYLATE)S PREPARED BY GTP

Alkyl ester group	MW (calculated)	<Mn>	GPC* <Mw>/<Mn>
t-butyl	25,000	33,200	1.31
2-ethylhexyl	25,000	30,900	1.32
methyl	25,000	31,400	1.07

* Based on PMMA stds.in THF

Copolymer	Block MW (calculated)	GPC <Mn> (g/mol)			<Mw>/<Mn>	
		1st	2nd	3rd		
MMA-b-tBMA*	5k-5k	--	--	7,850	1.16	
	30k-30k	--	--	23,650	1.28	
MMA-2EHMA-MMA**	sequential	6k-48k-6k	8,400	42,600	42,800	1.56
	coupling	6k-48k-6k	8,400	--	26,700	1.31

* Based on PS stds.in THF

** Based on PMMA stds.in THF

Table 19: Microstructure of various Alkyl methacrylate Homopolymers

Ester alkyl group	Temp. (°C)	‡Tacticity			Catalyst
		I	S	H	
methyl	50	9	40	51	TBAB
	33	7	48	45	TBAB
	10	5	49	46	TBAB
	40	8	54	38	TASHF ₂
	25	7	56	37	TASHF ₂
	0	7	58	35	TASHF ₂
	-78	4	65	31	TASHF ₂
t-butyl	--	--	--	--	TBAB
2-ethylhexyl	--	--	83	17	TBAB

The values reported for the GTP of MMA using two different catalysts were obtained under controlled temperature conditions. The syndiotactic triad composition, determined from ^1H NMR, increases with decreasing temperature, primarily at the expense of the heterotactic sequences. The values reported for the GTP of PMMA using TASHF_2 were obtained by controlling the polymerization temperature through external heating and cooling sources (e.g. water baths). These values correspond within experimental error to those reported for similar temperatures by other investigators [77,125,126]. The syndiotactic triad composition data for polymerizations carried out with TBAB is lower than expected, though the same trend of increasing syndiotactic content with decreasing temperature is observed. No conclusive argument for this difference can be made with such a minimal amount of information, except that the temperature was more accurately controlled. These values, obtained using TBAB, stem from kinetic investigations in which the polymerization reactor temperature is controlled using a solanoid cell capable of maintaining a set value (± 2 °C).

In order to demonstrate the living nature of GTP, all-methacrylic ester block copolymers were prepared. Depending on the nature of the ester alkyl substituent a diverse group of multicomponent systems can be prepared with unusual properties. Using sequential addition techniques,

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copolymers of MMA with either *t*-butyl methacrylate or 2-ethylhexyl methacrylate were prepared. The efficiency of this technique is dependent on the reactivity of the monomer but more importantly the purity of each monomer. Any impurities in subsequent monomer additions will lead to homopolymer contamination. Hence, the monomers were carefully purified using trialkyl aluminum or trialkyl aluminum/dialkyl aluminum hydride purification reagents as indicated in Chapter 3.

The GTP of each monomer proceeded for one hour prior to the addition of another monomer or terminating reagent to the living polymerization. Methyl methacrylate was polymerized in all cases as the first block. With numerous investigations showing that an hour was sufficient to ensure complete conversion of MMA at these molecular weights and catalyst level, a second monomer was charged. It is evident from the low incorporation of *t*-butyl methacrylate determined by NMR, and conversions that these polymerizations were prematurely terminated before complete conversion.

Copolymers having a center block of 2-ethylhexyl methacrylate were also prepared using sequential addition and coupling techniques. Characterization of these materials is summarized in Table 18B. For the triblock copolymer obtained via sequential addition techniques, the molecular weights of diblock and triblock copolymer

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correspond. The presence of a significant amount of low molecular weight tailing in the GPC trace of the final triblock due to premature termination is weighted in the $\langle M_n \rangle$ value, therefore an obvious molecular weight increase indicating the polymerization of the final aliquot of MMA is not readily apparent. The efficiency of coupling of PMMA-b-P2EHMA diblocks was difficult to determine since a sample was not removed from the reaction vessel prior to the coupling step and the strong odor of 2-ethylhexyl methacrylate monomer was evident during isolation indicating incomplete polymerization of the second monomer. Though the copolymer average molecular weight and composition was not accurately determined, additional characterization involving differential scanning calorimetry (DSC) was performed (Table 18B). The evidence of two glass transition temperatures (T_g) indicates the presence of microphase separation in these copolymers. More defined synthesis of a series of materials ranging in composition, and further characterization of these materials using analytical tools, such as DMTA, would elucidate the thermoplastic behavior of these materials.

FUNCTIONALIZED MATERIALS. An alternative method of preparing well defined multicomponent systems is via functionalized oligomers. The use of GTP to prepare functionalized chelic and telechelic polymers has been

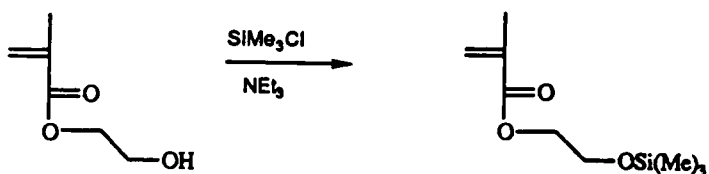
reviewed by F.P. Boettcher [64]. The success of the preparation of end functional polymers in living systems is dependent on the purity and reactivity of reagents, and the absence of terminating side reactions and chain transfer. It was our intent to prepare functionalized oligomers of PMMA by GTP to be used as building blocks in subsequent post reactions.

It was of interest to prepare block copolymers of PMMA and poly(propylene oxide) (PPO) via a transformation reaction from the GTP mechanism to Aluminum porphyrin mechanism [193]. This transformation reaction can be extended to the preparation of a novel thermoplastic elastomer having PPO as the center block. Variation of the components immediately gives rise to other unusual multicomponent systems. For instance, copolymers based on 2-ethylhexyl methacrylate and isobutyleneoxide leads to a system having a semi-crystalline component. To explore the feasibility of this transformation process hydroxyl functional oligomers of PMMA were prepared via GTP.

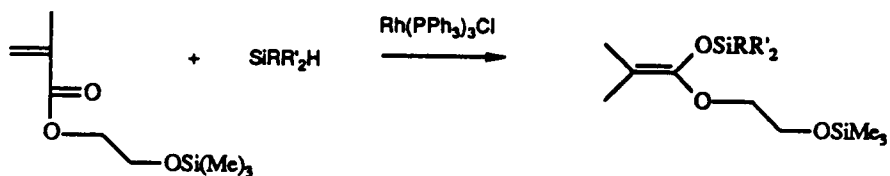
To prepare oligomers having hydroxyl functionality a protected initiator was prepared as shown in Scheme 17. Since GTP is sensitive to protic impurities, it is necessary to protect the hydroxyl functional group of 2-hydroxyethyl methacrylate. Upon isolation of the protected material, 2-(trimethylsiloxy)ethyl methacrylate, a hydrosilylation reaction to prepare the functionalized ketene silyl acetal

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1) PROTECTING STEP



2) HYDROSILYLATION



$\text{R}' = \text{ethyl or methyl}$

Scheme 17. Synthesis of Protected Hydroxyl GTP Initiator

was then performed in the presence of Wilkenson's catalyst. Each step leading to the preparation of the functionalized initiator was followed via ^1H NMR (Figure 9). The disappearance of the vinyl protons (A) and the appearance of two singlets corresponding to the protons of the β methyl groups (D,E) conveniently shows the formation of the desired product.

Homopolymers of PMMA were prepared using TBAB as the selected catalyst. Initiation of the GTP of MMA using this protected initiator easily allows the synthesis of primary hydroxyl functionalized PMMA after hydrolysis of the protecting group. By the nature of transformation reactions, the oligomers could be characterized prior to the post reaction [Table 20]. Investigations are continuing with respect to optimization of the crossover reaction from GTP to aluminum porphyrin mechanism with these hydroxyl functional materials.

It was also desired to prepare oligomers having a different reactive chelic group, such as carboxylic acid functionality. A protected ketene silyl acetal based on methacrylic acid had been reported previously by DuPont workers [77]. During the preparation of this initiator, isolation of the pure product was difficult due to the extreme instability of the substance, hence, an alternative starting material, *t*-butyl methacrylate, was selected to prepare carboxylic acid functionalized oligomers. Due to

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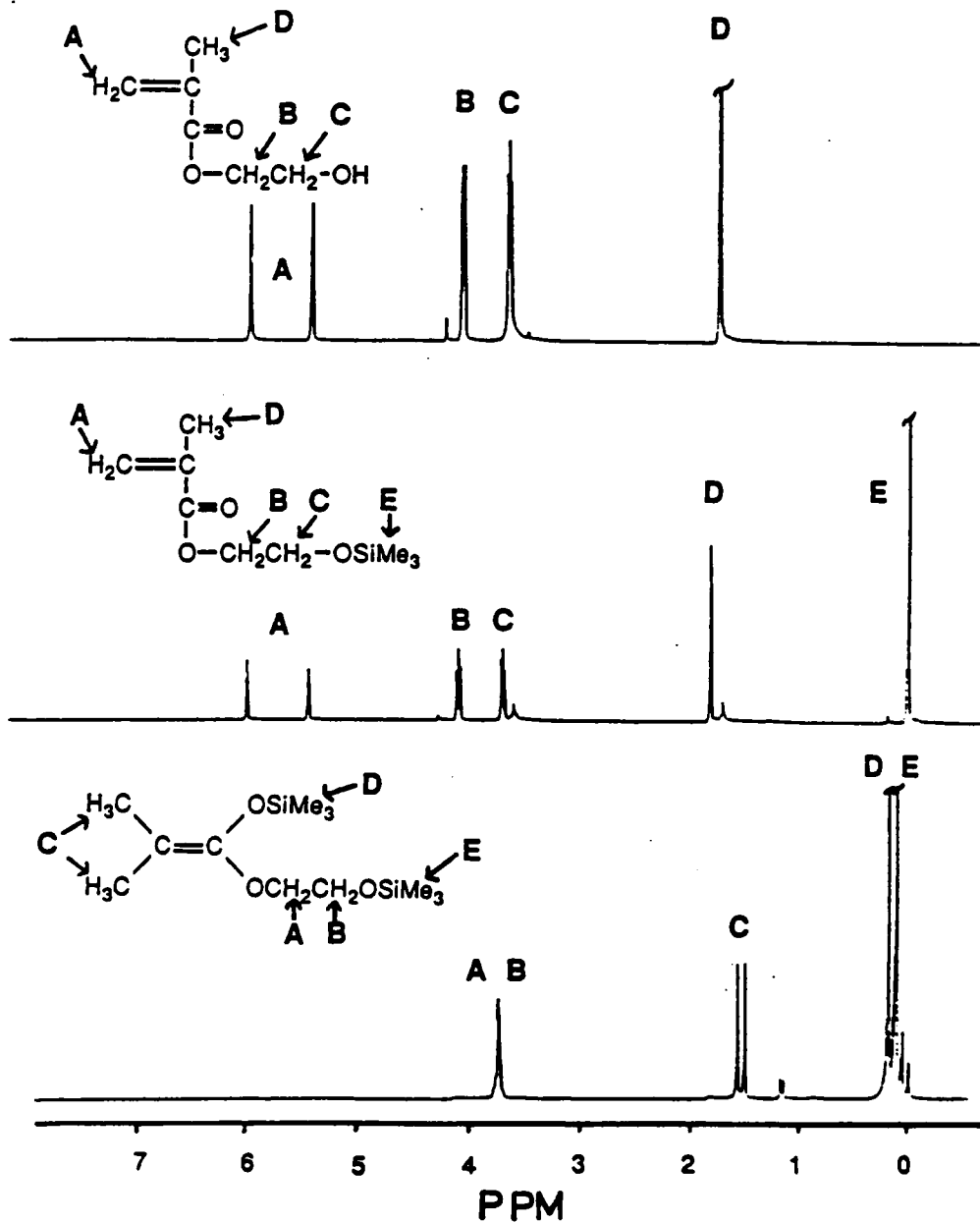


Figure 9. ^1H NMR of the Formation of Protected GTP Initiator

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TABLE 20: CHARACTERIZATION OF PMMA FUNCTIONALIZED OLIGOMERS

Entry	MW (calculated)	GPC ^a		VPO ^b
		<Mn>	<Mw>/<Mn>	
1	1,000	1,500	1.13	-----
2	5,000	6,300	1.11	6,700
3	10,000	-----		11,700
4	20,000	20,300	1.10	-----

^a Based on PMMA stds

^b Toluene at 63 °C

the ease of acid hydrolysis of the t-butyl ester group, chelic oligomers would be easily prepared. Use of this initiator also presents a means to prepare chelic and telechelic ionomers.

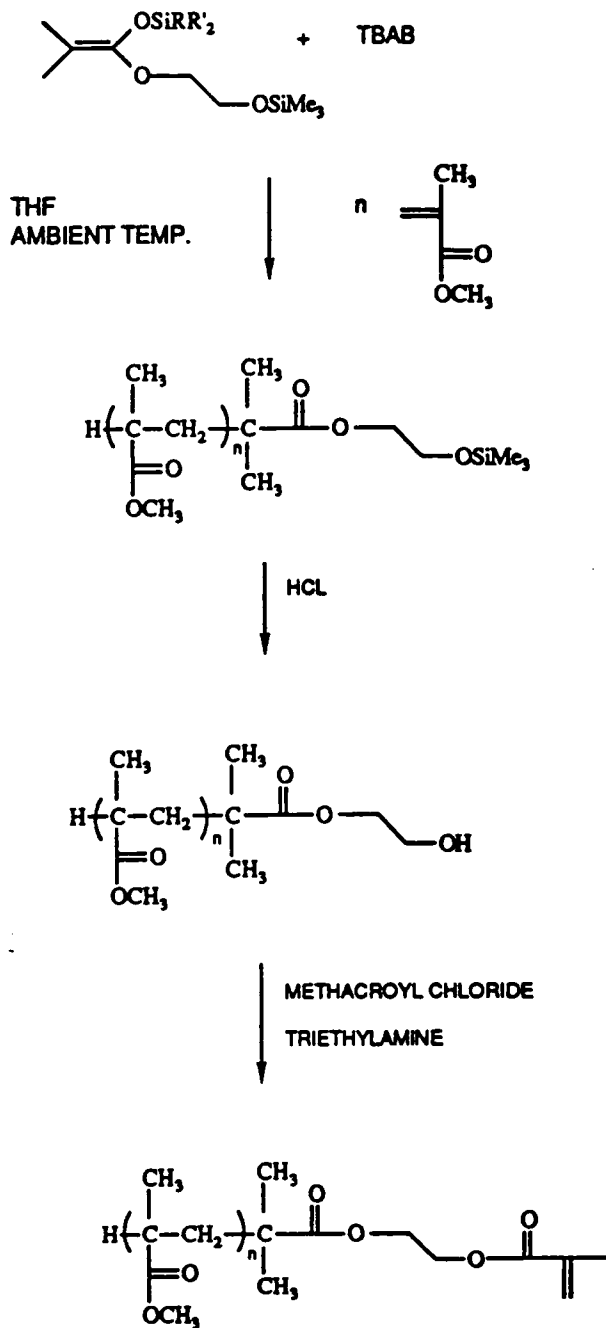
The protected initiator was prepared from the direct hydrosilylation of purified t-butyl methacrylate. Due to the unfortunate lack of instrumentation, primarily NMR, during the preparation of this initiator, quantitative formation of the ketene silyl acetal as well as purity of the reagent could not be accurately determined. Subsequent use of this initiator for the GTP of MMA resulted in low yields (< 10%). The presence of impurities from the synthesis of the initiator or the slow initiation of monomer due to electronic effects or the presence of the bulky t-butyl group may be responsible for the poor conversion. It is difficult however to project without sufficient characterization of the initiator. If indeed slow initiation relative to propagation inhibits the polymerization it may be of interest to elucidate whether electronic or steric effects are the primary influence. Experiments comparing t-butyl and neopentyl methacrylate based initiators may elucidate some interesting results. Though neopentyl methacrylate possesses a bulky ester moiety, the electronic nature or basicity of the carbonyl oxygen is similar to MMA in contrast to t-butyl methacrylate.

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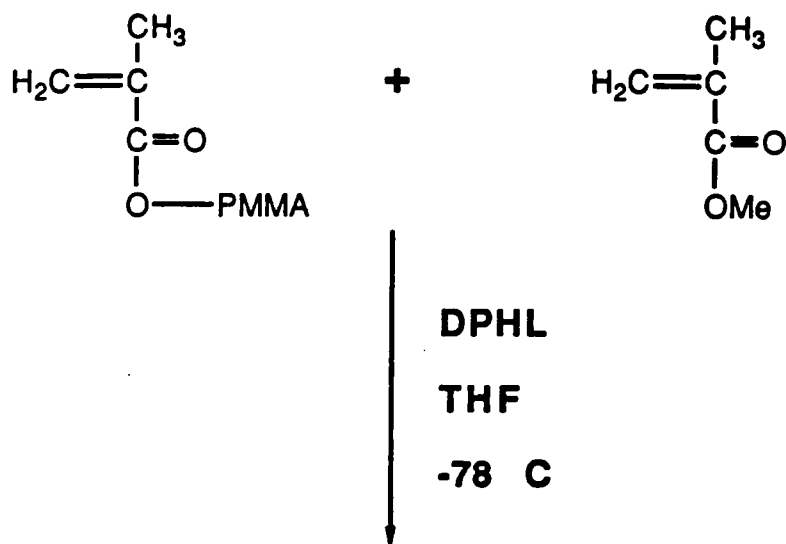
Though the use of the hydroxyl functional materials was not sufficiently optimized for the proposed transformation reaction, they were of value for another investigation. J.M. DeSimone proposed a multidisciplinary study involving the synthesis of model branched copolymers and classical characterization techniques to determine the accuracy of the "universal" calibration method used in size exclusion chromatography [194,195]]. The use of GTP in this collaborative effort was in the preparation of PMMA macromers, which, upon copolymerization with MMA yields well-defined graft polymers containing nearly monodisperse branches.

The PMMA oligomers prepared by GTP were reacted with methacryloylchloride to afford methacryloxy functionalized PMMA macromonomers (Scheme 18). Copolymerization of the macromonomer could easily proceed using three different mechanisms; anionic, GTP, and free radical. Anionic techniques were conveniently employed to ensure the preparation of monodisperse graft copolymers with Poisson distribution of molecular weights (Scheme 19). Figure 10 illustrates the presence of unincorporated PMMA macromonomer, which was removed via fractionation [195]. The traces do indicate the preparation of graft copolymers having peak molecular weights centered around 160,000 g/mole and narrow polydispersities relative to linear PMMA standards [194].

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Scheme 18. Synthesis of PMMA Macromer by GTP



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Scheme 19. Anionic Synthesis of PMMA-g-PMMA

RESULTS AND DISCUSSION

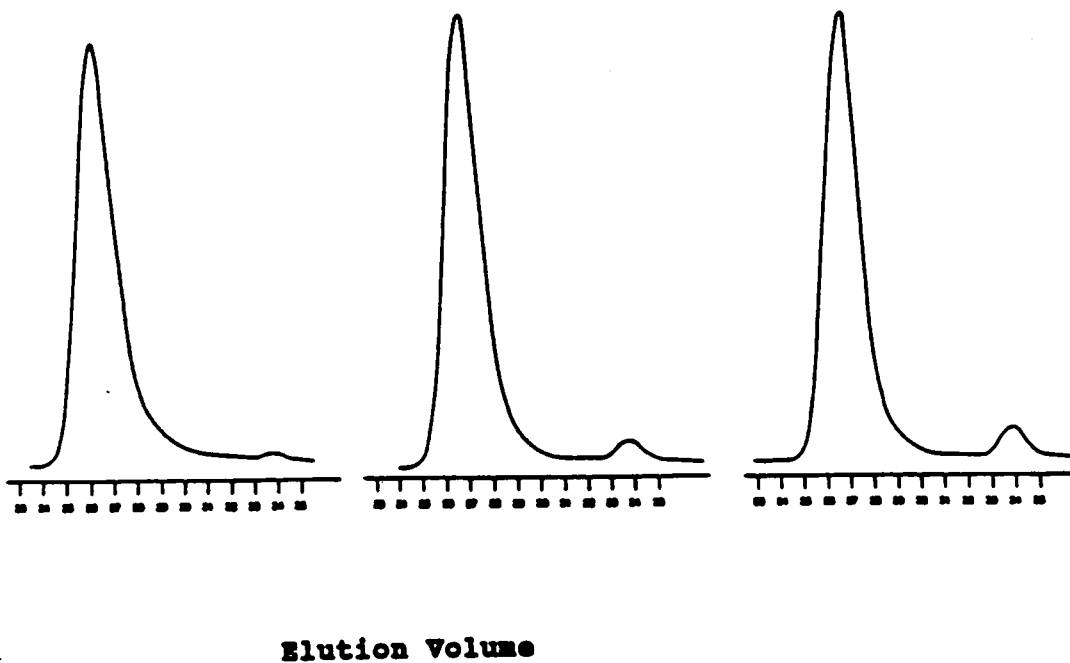
GPCs OF PMMA-g-PMMA (UNFRACTIONATED)

Figure 10. PMMA-g-PMMA Size Exclusion Chromatography

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Other investigations involving the preparation of functionalized oligomers were in the utilization of novel termination reactions. Though Asami et al., [81] illustrated the termination of GTP with vinylbenzylbromide, our interest was directed to termination with vinylbenzyl iodide or -chloride for the purpose of preparing PMMA-b-PDMS copolymers via coupling reactions. Vinylbenzylchloride functional PDMS oligomers were prepared and characterized, and this will be further addressed later in this chapter. Prior to the termination of living PMMA, an attempt was made to exchange chloride for iodide using sodium iodide. The exchange of the halides on the PDMS chain end was not characterized prior to termination of the PMMA chain end with the siloxane oligomers thus, the efficiency of the halide exchange was unknown. However, characterization of the PDMS terminated PMMA indicated the incorporation of some siloxane (3-5%). Studies using vinylbenzylchloride were begun in order to optimize the in situ exchange reaction. Other investigations involved the termination of PMMA with phenylmaleimide derivatives for the preparation of functional oligomers having potential use in condensation reactions. The inherent pink color imparted to the polymer and evidence of aromatic proton resonances in the NMR indicated the incorporation of the maleimide into the polymer backbone. Since it has been documented that maleimides will polymerize by GTP [90] it would be more

RESULTS AND DISCUSSION

practical to prepare a maleimide based initiator for the preparation of chelic and telechelic oligomers.

KINETIC INVESTIGATIONS USING TBAB AS THE SELECTED CATALYST

INTRODUCTION. In order to gain more insight into the polymerization of MMA by GTP and the synthesis of multicomponent systems in which GTP was utilized as one of the mechanisms, kinetic investigations were pursued. A number of investigations, including kinetic [122-124,196] and labeling studies [115], have been conducted to establish the mechanism of GTP. These studies, reviewed in chapter 2, have focused on nucleophilic catalysts, in particular bifluoride and fluoride based catalysts. These have inherently lower solubility in THF, one of the common polymerization solvents, and the presence of a polar solvent such as acetonitrile is often required.

Currently, our work entailed investigations of the GTP of MMA in the presence of dimethyl(methyltrimethylsilyl)-ketene acetal (MTS) as the initiator and tetrabutylammonium benzoate (TBAB) as the selected catalyst. The benzoate catalysts, in comparison to the traditional fluoride catalysts, are soluble in the polymerization solvent THF. With this soluble catalyst and the aid of a low pressure "living" polymerization reactor we were able to explore the

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effect of both the benzoate catalyst and initiator concentrations on the rate of polymerization while maintaining strict temperature control. It was of interest to gain more insight on the activity and role of this particular catalyst since it was the catalyst of choice for the polymerization of multicomponent systems by GTP in the presence of poly(dimethylsiloxane). This concept of catalyst selection will be addressed in the discussion of block copolymers of PMMA and PDMS.

METHODOLOGY AND SAMPLE ANALYSIS. The kinetic investigations were carried out in a controlled temperature polymerization reactor and the conditioning process of this reactor prior to the experimental investigations is fully described in Chapter 3. These reactors have been utilized extensively in our laboratories for the polymerization of alkene monomers; dienes, styrene, and alkyl methacrylates by anionic polymerization methods. The extension of the use of this reactor to GTP permits the study of the influence of catalyst, initiators, and monomer concentrations, solvent and temperature on the rates of polymerization while maintaining stringent reaction conditions for the polymerization. GTP exhibits a detectable exotherm even with very dilute solutions, hence, it was necessary to restrict the polymerization exotherm in order to isolate the effects of different variables on the reaction that may be

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over-shadowed or complicated by variations in reaction temperature. The reactors were equipped with coils through which a steam water mixture could flow for precise control of the temperature of polymerization. Thus, it was possible to independently determine the effect of catalyst level, and initiator concentration on the polymerization rate and consequently the effect of temperature at a constant catalyst level.

To examine these variables, samples were removed from the reactor with time through the dip-tube into purged vials containing methanol for quenching the polymerization reaction. An aliquot of each quenched sample was removed by syringe to prepare NMR samples in d-chloroform. The samples were analyzed using a Bruker WP 270 MHz instrument. Figure 11 depicts a typical NMR trace of the sample solution. As noted from the spectra, there is no significant interference from the solvent peaks. This enables the conversion of monomer to polymer to be obtained through selective ratioing of the integration of peaks due to the vinyl protons of the monomer and the α -methyl protons of the polymer backbone. This is effectively illustrated in Figure 12 showing a stacked plot which demonstrates the destiny of the peaks arising from the aforementioned regions with time. The remaining portion of each sample, not utilized for NMR analysis, was stripped, dried to remove unreacted monomer and solvent, and analyzed by GPC. Manifested by the GPC

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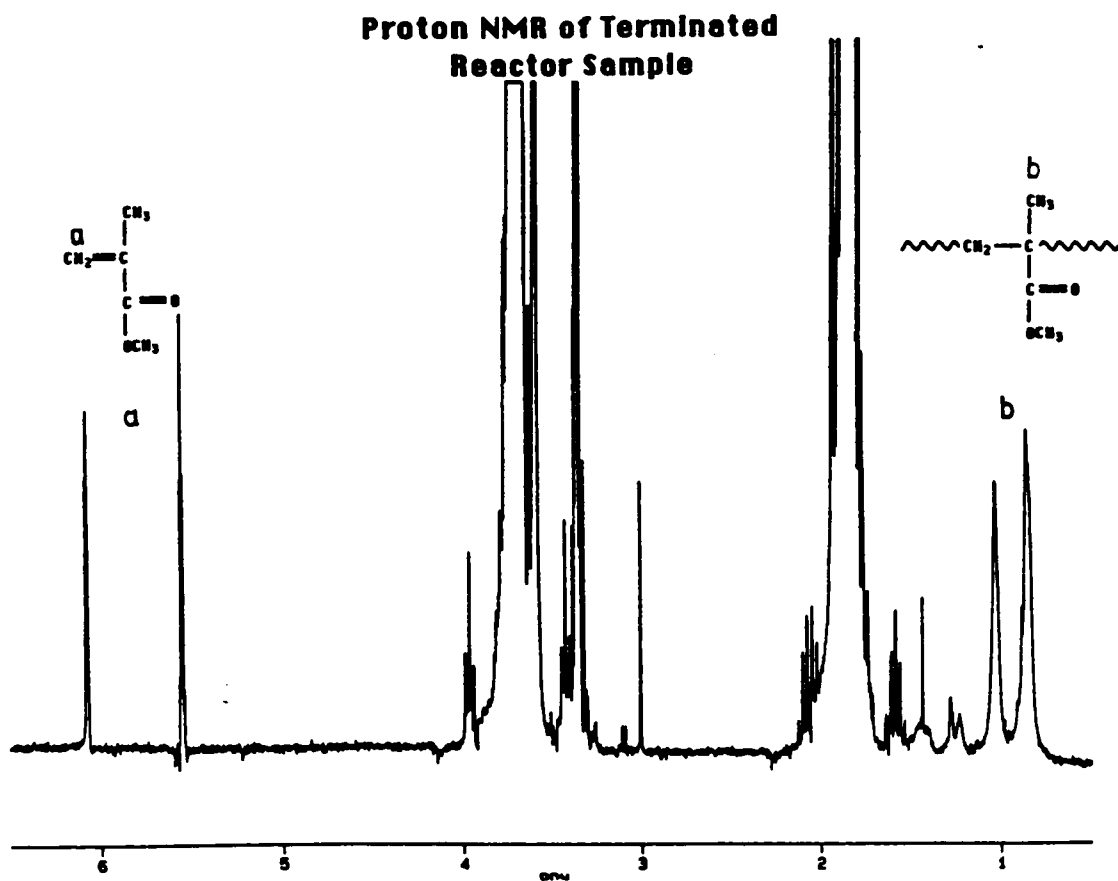


Figure 11. ^1H NMR of Sample Solution during Kinetic Investigations.

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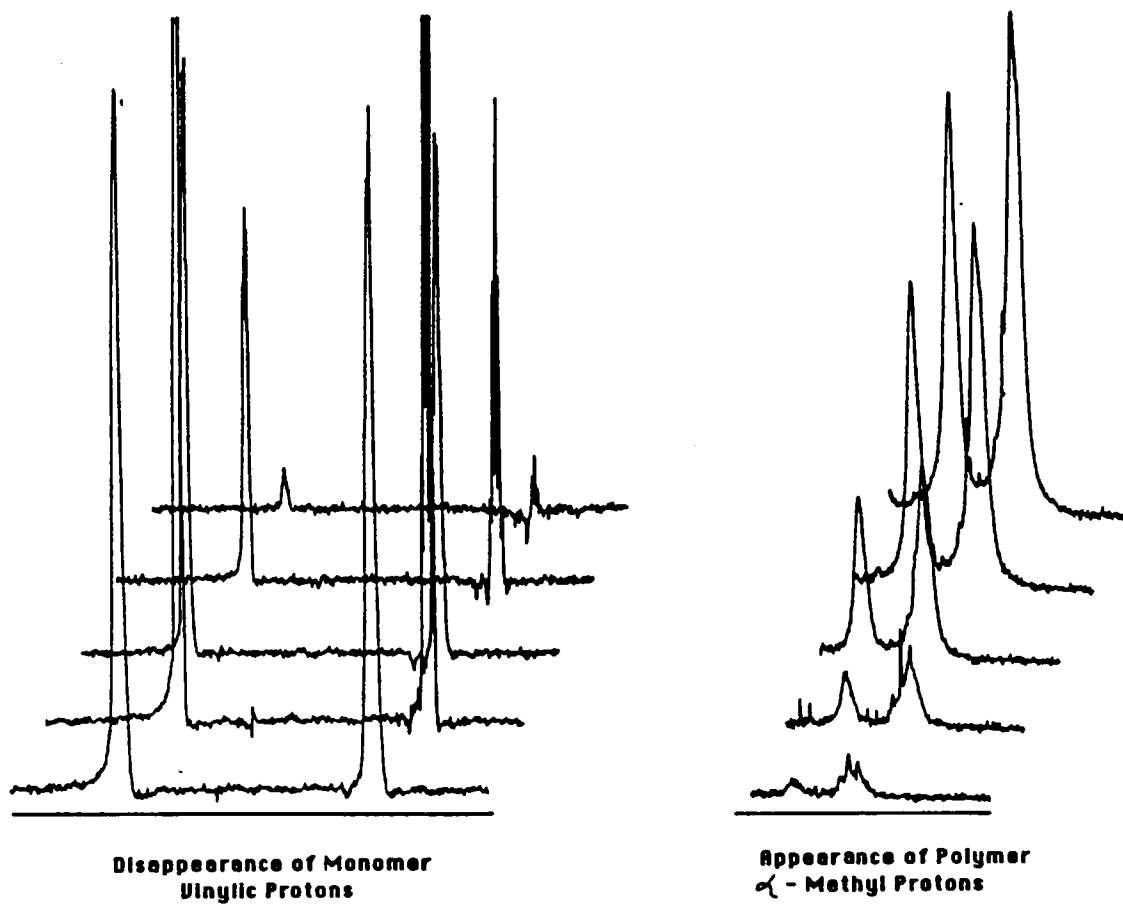


Figure 12. Stacked ^1H NMR Spectra of Conversion with Time.

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traces shown in Figure 13 is the shift of the traces to lower elution volumes with time. This is indicative of increasing molecular weight with conversion of monomer to polymer.

This experimental procedure was repeated at various concentrations of initiator, catalyst, and at different temperatures. The results obtained will be presented in the following sections and compared to the results obtained by other investigators. Indeed, it is important to preface the discussion of the kinetic results with mention of the ability to compare results. Each investigator has been working with a different mode of addition of reactants, variable concentrations and types of reactants, and different methods of analysis. Therefore, direct comparisons are difficult and may be questionable based on first principles, but some correlations concerning the various trends may be possible.

INTRODUCTION TO THE KINETIC RESULTS. At a constant temperature, the rate of any reaction is expressed in terms of the existing concentration of the reactants [197]. For GTP, using the kinetic scheme established by Mai and Müller [123] for the duPont associative mechanism, the rate of polymerization can be expressed as Equation 20.

$$R_p = -d[M]/dt = k_p [M]^\alpha \cdot [I]_0^\beta \cdot [C]_0^\tau \quad \text{Eq. 20}$$

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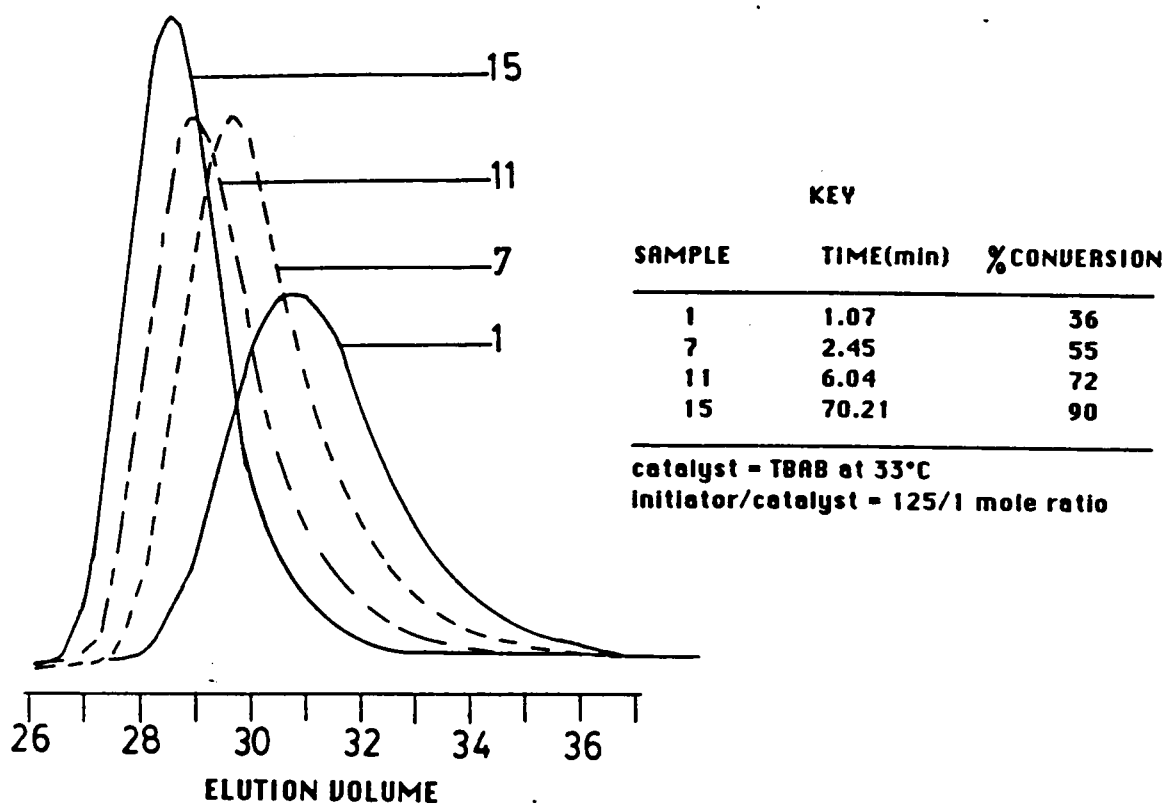


Figure 13. Conversion vs Time Visualized by Stacked GPC Traces.

Derivation of this expression was outlined in Chapter 2. The degree dependence of the rate of propagation on reaction concentration is known as the kinetic order of the reaction. The kinetic order of a reaction is determined experimentally and represents the fitting of the experimental data to the rate equation for the reaction in question. The magnitude of each exponent is commonly stated as the order of reaction in that species [197-199]. Determination of the order of reaction in each reactive species [Eq.20] requires the determination of the initial rate at various concentrations of reactants; monomer, catalyst and initiator. Putting Eq. 20 into logarithmic form,

$$\log([M]/dt) = \log k_p + \alpha \log[M] + \beta \log[I] + \gamma \log[C] \quad \text{Eq.21}$$

it becomes evident that using a bilogarithmic plot one can elucidate the reaction order with respect to a specific reactive species. It was our aim to elucidate the order of reaction with respect to the TBAB catalyst and MTS initiator.

DEPENDENCE OF REACTION RATES ON CATALYST CONCENTRATION.

Our studies began with the investigation of the dependence of reaction rate on catalyst concentration (Table 21). The concentration of the catalyst, TBAB, was varied from 1.2 x

TABLE 21: DATA PERTAINING TO KINETIC STUDIES*

Study 1: Variation of $[C]_0$ at constant $[I]_0$ and Temp. = 33 °C

$[I]_0$ ($\times 10^9$)	$[C]_0$ ($\times 10^9$)	$[I]_0/[C]_0$	k_{app} ($\times 10^9$)	$\log(k_{app})$
1.84	12.23	15/1	38.00	-1.42
1.84	2.45	75/1	2.83	-2.69
1.84	1.23	150/1	1.30	-2.89

Study 2: Variation of $[I]_0$ at constant $[C]_0$ and Temp. = 33 °C

$[I]_0 \times 10^3$	$[C]_0 \times 10^5$	$[I]_0/[C]_0$	$k_{app} \times 10^3$	$k_p'^{**}$	$\log(k_p')$
4.89	2.45	199.52/1	2.1	85.71	1.93
3.68	2.45	153.17/1	4.9	200.00	2.30
1.22	2.45	49.80/1	11.0	448.98	2.65

Study 3: Variation of $[I]_0$ & $[C]_0$ at a constant $[I]_0/[C]_0$ ratio and Temp. = 33 °C

$[I]_0$ ($\times 10^3$)	$[C]_0$ ($\times 10^5$)	$[I]_0/[C]_0$	k_{app} ($\times 10^9$)	$\log(k_{app})$	$k_p'^{**}$	$\log(k_p')$
3.68	2.45	150/1	4.9	-2.31	200.00	2.30
1.84	1.22	150/1	1.3	-2.89	106.56	2.03
1.22	0.82	150/1	0.83	-3.08	101.59	2.00

Study 4: Variation in temperature:

Temp	1/T (°K)	$[I]_0$ ($\times 10^3$)	$[C]_0$ ($\times 10^5$)	$[I]_0/[C]_0$	k_{app} (10^9)	$k_p'^{**}$	$\log(k_p')$
10	.0035	1.84	1.22	150/1	0.23	18.85	1.27
33	.0032	1.84	1.22	150/1	1.30	106.56	2.03
50	.0031	1.84	1.22	150/1	2.10	172.13	2.24

* $[M]_0 = .919$ M for all studies.** $k_p' = k_{app}/[C]_0$

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10^{-4} to 1.2×10^{-5} M. Each experiment was conducted at 33 °C under 30 psig of nitrogen. The order of addition of reagents was as follows. First, addition of initiator, MTS, to the polymerization solvent THF. Followed by the addition of a calculated aliquot of the catalyst solution (4 M). Catalyst and initiator were permitted to complex prior to the fast charge of monomer. The time allotted for initiator and catalyst to complex was consistently 5 min., though no experimental evidence was established that this amount of time was necessary or sufficient to permit the equilibria formation of the activated initiator-catalyst complex.

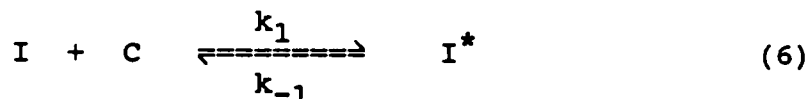


Figure 14 illustrates the first order plots for the conversion of monomer at various catalyst concentrations. The apparent rate constant (k_{app}) for each catalyst concentration was determined using the method of initial rates [199]. This method is facilitated by having one reactant present in much greater concentration than the others. This is easily achieved for kinetic studies involving polymerization mechanisms since usually the monomer concentration greatly exceeds the concentration of initiator, or as in GTP, also the catalyst concentration. The method of initial rates requires a sensitive analytical

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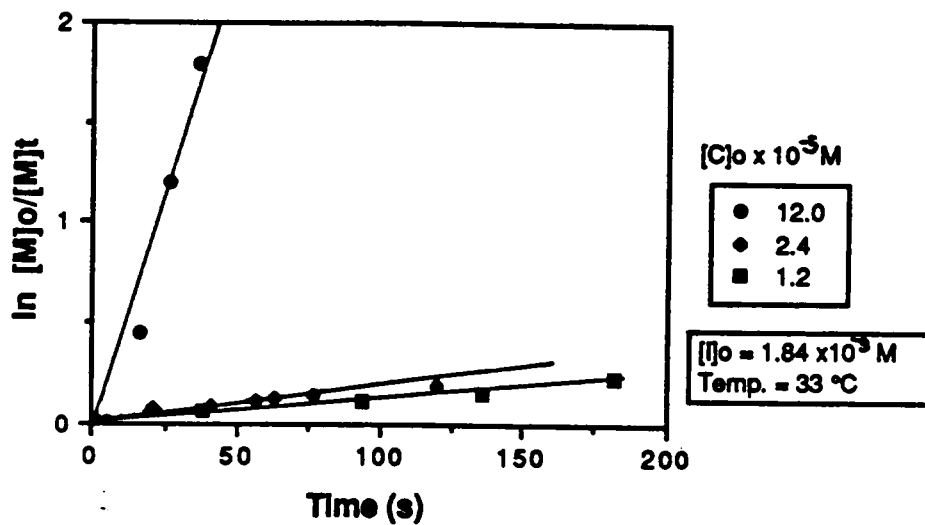


Figure 14. First Order Plots for Conversion vs Time at Various Concentration of TBAB

RESULTS AND DISCUSSION

method such as spectroscopy for the determination of reactant or product concentrations. It should be noted that a disadvantage of the method of initial rates with at least one reactant in severe deficiency relative to the others is its sensitivity to reactive impurities present in the reactants having higher concentration, [197,199] e.g.; monomer or in the solvent. This is a critical consideration when evaluating "living" polymerizations since the presence of reactive impurities may lower the concentration of active chain ends and thus, alter the concentration of reactants relative to one another which would destroy the living character. To minimize the influence arising from extraneous impurities present in solvent and reagents, specifically monomers, these were carefully purified as described in the experimental section (Chapter 3).

Following from equations 20 and 21, a bilogarithmic plot of the apparent rate constants obtained from the maximum slope, i.e. initial rates, of the first order time-conversion curves vs the various catalyst concentrations was constructed (Figure 15). The k_{app} for the high level of catalyst (1.2×10^{-4} M) could not be determined accurately. At this concentration of catalyst, the temperature control system of the reactor was unable to control the exotherm of polymerization and maintain the strict temperature control of 33°C necessary for this kinetic investigation. During this particular run the temperature was recorded to have

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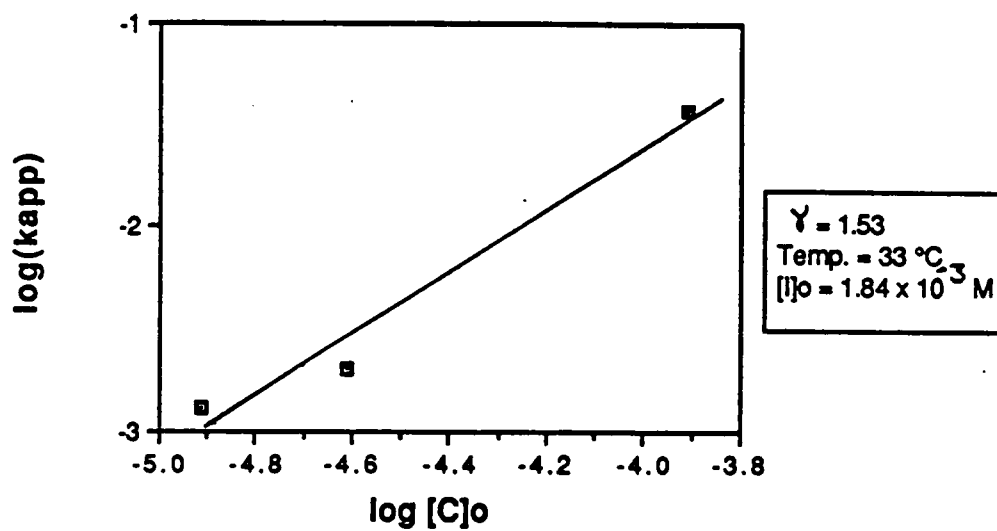
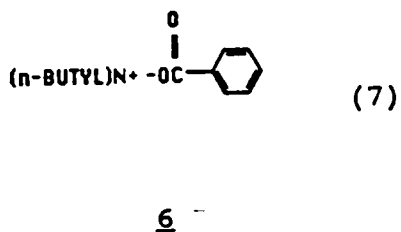
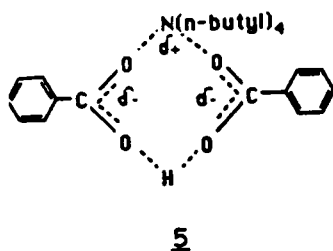


Figure 15. Bilogarithmic Plot of k_{app} vs Concentration of TBAB

increased to 41 °C, which brings out another point. The concentration range of initiator and catalyst which can be studied is limited by the experimental considerations such as sampling speed and temperature control in addition to the level of impurities.

The value for the reaction order, γ , with respect to catalyst concentration was determined to be 1.53. Loss of temperature control could significantly affect the apparent rate constant causing deviation from the proposed first order dependence with respect to catalyst concentration. It was important to dismiss any other possible explanations for the observed deviation in the reaction order.

In the utilization of the benzoate catalyst it is important to keep in perspective that during the preparation some bibenzoate product may be prepared (structures 5).



(7)

In kinetic investigations the presence of an alternate catalytic species, which may be more reactive than the catalyst under investigation, may cause some discrepancy in the observed apparent reaction rates and the determined

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reaction order. With this possibility in mind, the catalyst utilized in these investigations was thoroughly characterized by elemental analysis (Table 22) and ^1H NMR (Figure 16). Integration of the aromatic protons relative to the protons arising from the methyl or methylene protons of the tetrabutylammonium group indicates the absence of bibenzoate catalyst. Within the limits of experimental error it can be shown from elemental analysis that the monobenzoate, TBAB, is the only catalytic species present, though indication does suggest that the sample had acquired some water prior to the analysis. With the characterization demonstrating the presence of only one catalytic species, TBAB, it was determined that the deviation in the predicted value of \bar{Y} from 1 may be influenced by the loss of temperature control in the experiment using a high level of catalyst.

It is difficult to directly compare these results to those reported by other investigators since the catalyst systems and concentrations are different. Table 23 lists some of the information reported by Brittain and Müller et al. It is important to note, that our results as those of Müller, reflect average propagation rates, unlike the study conducted by Brittain which focused on isolating the reaction order dependence of various catalysts on initiation and first and second propagation steps. It is also again apparent from this summary of data, that each investigator

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TABLE 22: ELEMENTAL ANALYSIS OF TETRABUTYLAMMONIUM
BENZOATE (TBAB)

	%C	%H	%N	%O
Calculated	76.19	11.12	3.87	8.82
Analysis ^a	72.14	11.06	3.33	13.75

^a Performed at Galbraith Laboratories

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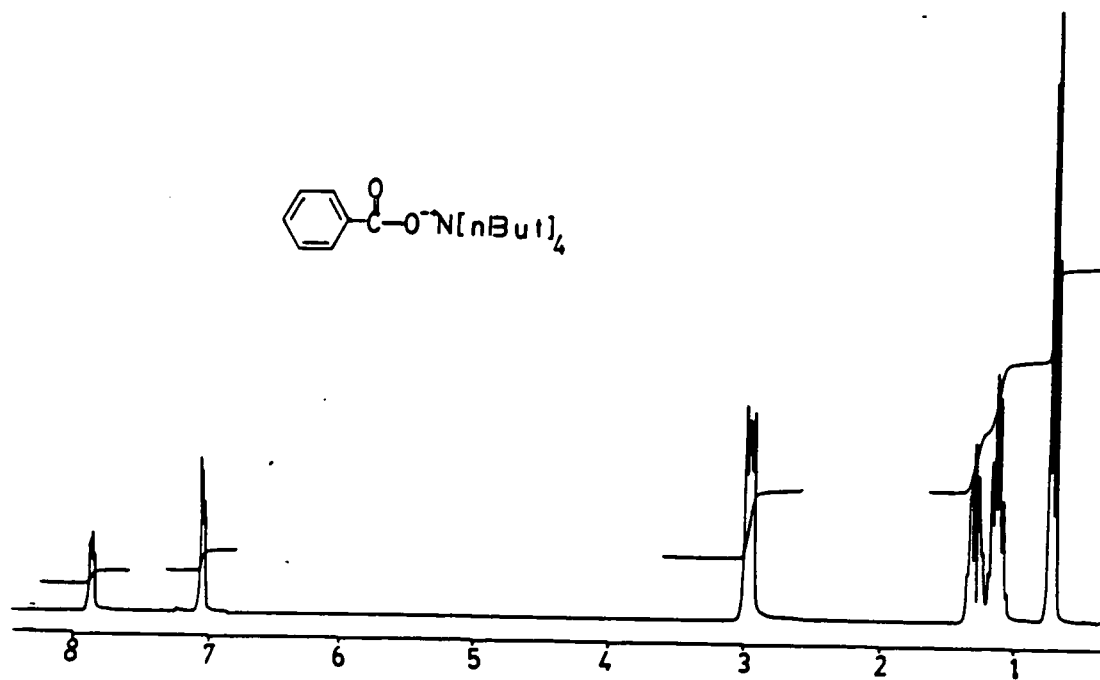


Figure 16. ^1H NMR of Tetrabutylammonium Benzoate

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TABLE 23. SUMMARY OF OTHER REACTION ORDER RESULTS FOR THE GTP OF MMA

Catalyst	Concentration Range (M)	Reaction Order (τ)	Ref.
TPSHF ₂	.0025-.005	2	196
TASHF ₂	.001-.00025	2.1	196
TPSBz	.008-.00013	1	196
TBABB	.001-.005	0.3	196
TASHF ₂	1×10^{-5} - 7.5×10^{-5}	1.17	123
TASBz	--	-0.3 to +1.0	125

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is evaluating GTP with varied conditions; reagents and their purity, concentrations of reagents, temperature, and mode of addition. These variables make it difficult to accurately compare experimental data.

REACTION ORDER WITH RESPECT TO INITIATOR CONCENTRATION.

In the same manner as described above the reaction order with respect to initiator concentration was evaluated for the GTP of MMA. The concentration range examined spanned from 4.89×10^{-3} to 1.2×10^{-3} M. Again the first order plots for these concentrations were constructed and the apparent rate constants determined via the initial slope method (Figure 17). For determination of initiator reaction order, β , the "psuedo" rate constants, k_p' , were calculated by Equation [22].

$$\log k_p' = \text{const} \cdot \beta [I]_0 \quad \text{Eq.22}$$

$$\text{where } k_p' = k_{\text{app}}/[C]_0$$

Figure 18 shows a plot of $\log k_p'$ vs $\log [I]_0$. The slope or value of β obtained was not in accordance with the kinetic scheme proposed by Mai and Müller. A value of -1.06 is obtained for β representing the reaction order with respect to MTS concentration while maintaining a constant initial concentration of the TBAB catalyst.

Though, Müller et al., [125] reported a value of +1.0

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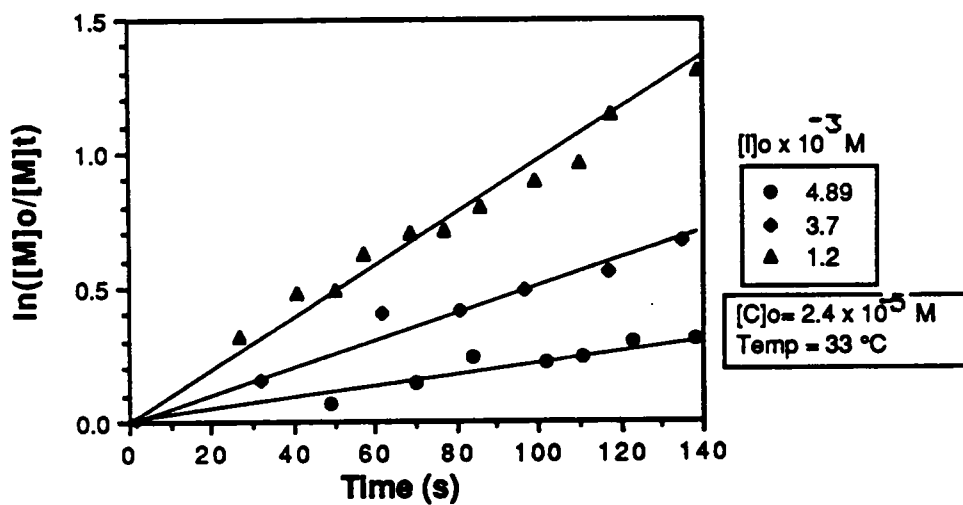


Figure 17. First Order Plots for Conversion vs Time at Various Concentration of MTS

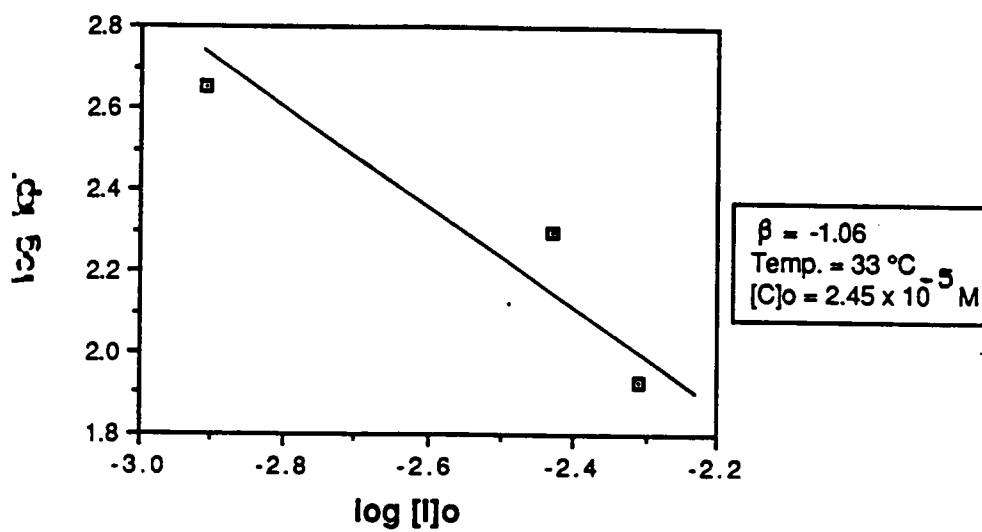


Figure 18. Bilogarithmic Plot of k_p' vs Concentration of MTS

for β in a concentration range 1.3×10^{-4} - 5.3×10^{-4} M for MTS using trisdimethylaminosulfonium benzoate, the concentration of catalyst used in this study was not reported therefore comparison to this data is difficult. In addition, a range of values for the reaction order with respect to concentration of this catalyst, γ , was reported which further complicates the evaluation.

In another study, in which the selected catalyst was TASHF₂ ($\sim 2.4 \times 10^{-5}$ M), Müller et al., reported a value of β -0.27 for MTS spanning a concentration range of 0.34×10^{-3} to 4×10^{-3} [123]. They proposed that the deviation from the proposed kinetic scheme indicated that the initiator inhibits the reaction. To account for this phenomenon an extended kinetic scheme was presented by Mai and Müller (Scheme 13). From this kinetic scheme it was proposed that either initiator or polymer may react with the activated initiator or polymer leading to an inactive product which is capable of binding catalyst. As understood from the proposed scheme, if the formation of such an inactive species were occurring, the number of active or propagating centers would decrease and this would be reflected in a loss of molecular weight control as well as a loss in the Poisson distribution.

An alternative explanation for the apparent negative reaction order is the relative amount of catalyst to initiator. That is, the mole ratio of initiator to

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catalyst. Ordinarily, one would expect that as the concentration of initiator is increased the rate should be enhanced reflecting this increase, however this is not the case in GTP. Since GTP is catalyzed, the concentration of activated initiator or propagating chain end is dependent on the concentration of catalyst. Furthermore, in the absence of terminating side reactions, it is assumed in living polymerization methods that all chains essentially grow or propagate at the same time. Applying this background to the anomaly observed in GTP, at high concentrations of catalyst relative to initiator, the catalyst has to ideally activate fewer initiator or propagating chain ends during some time, t , to maintain the living character of the mechanism. This may be reflected in a $k_{-1} < k_p[M]$. However, at lower concentrations of catalyst the requirements of living polymerization must still be maintained, yet the value of k_{-1} may become greater than or equal to $k_p[M]_0$ ($k_{-1} \geq k_p[M]$). Effectively, the catalyst has to be associated with more molecules of initiator in a given amount of time, hence it may or may not be complexed to the silicon atom a sufficient amount of time to permit the addition of a monomer unit thus, a decrease in the apparent rate is observed. From this explanation, one would predict that the observed rate of polymerization at a constant catalyst concentration, would decrease as the initial concentration of initiator is increased.

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An important factor to note is that a favorable range may exist and its limits may be catalyst specific. In a more defined statement, as the concentration of catalyst is reduced relative to initiator concentration it may no longer be able to function effectively as a catalyst. On the other extreme, as the catalyst level is increased it may actually serve as an inhibitor forming an unreactive complex which may be reflected in the loss of living character, i.e.; molecular weight control and narrow polydispersity. Initial studies using ^{29}Si NMR to identify the complexation of initiator to catalyst and subsequently, coordination of monomer, have elucidated the decomposition of initiator with tetrabutylammonium fluoride. This may or may not be observed with the benzoate based catalysts. A signal corresponding to the resonance of silicon atoms in hexamethyldisiloxane was observed when MTS was complexed to tetrabutylammonium fluoride in a 1/1 mole ratio. These spectra were accumulated and observed at different intervals over an hour period hence, a quantization of the amount of byproduct is not possible with the NMR parameters utilized.

EFFECT OF A CONSTANT CATALYST RATIO ON THE REACTION ORDERS WITH RESPECT TO INITIATOR AND CATALYST. Prompted by the results obtained for the aforementioned experiments, another set of kinetic experiments were obtained at 33 °C using a constant mole ratio of initiator to catalyst

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(150/1). The first order time conversion plots were constructed for the various concentrations of initiator and catalyst and the apparent rate constants were again determined using the initial slope method (Figure 19). Since both initiator and catalyst concentration were varied the bilogarithmic plots to determine the reaction order with respect to each species were constructed (Figures 20 and 21). Firstly, it is observed from the values of the apparent rate constants that the rate of polymerization increases as the concentration of initiator is increased at a constant initiator to catalyst level. From the bilogarithmic plot of the "psuedo" rate constant (k_p') vs initiator concentration ($[I]_0$) the slope corresponding to the reaction order is determined to be 0.65. This indicates that at this low level of TBAB catalyst relative to initiator, the equilibrium is shifted to the left hand side of Scheme 12. An interesting extension of this study would be to examine the shift in the value of β as the initiator and catalyst concentrations are varied at a different, though constant, initiator/catalyst mole ratio.

Furthermore, the bilogarithmic plot of the apparent rate constant vs catalyst concentration yields a value of 1.67. Unlike the previous studies using various catalysts in which temperature control was lost, the exotherm of polymerization was contained and constant temperature maintained in all runs. The values of 1.53 and 1.67 may

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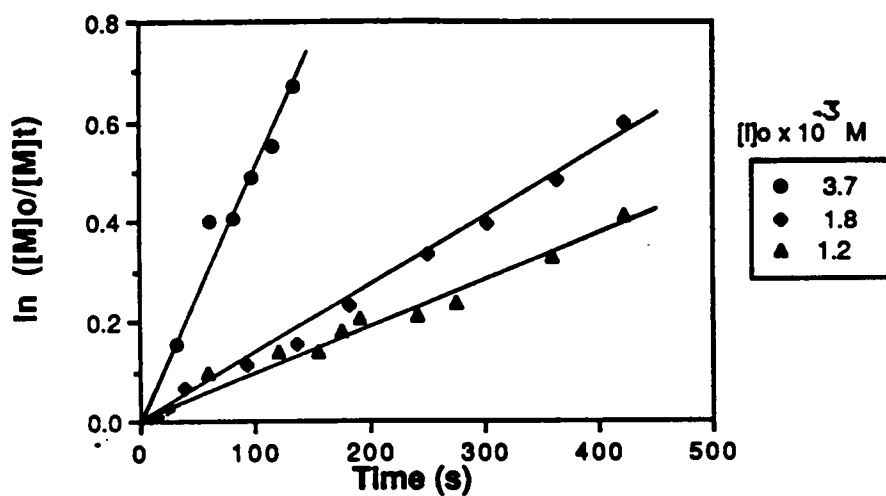


Figure 19. First Order Plots for Conversion vs Time for a Varying Concentrations of Initiator and Catalyst Maintaining a Constant Ratio of $[I]_0/[C]_0$

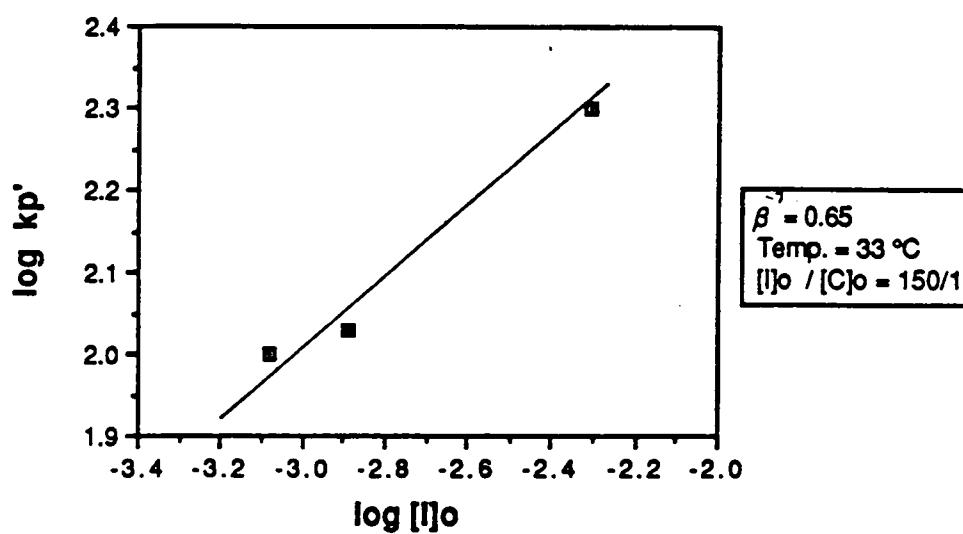


Figure 20. Bilogarithmic Plot of k_p' vs Concentration of MTS with a Constant Ratio of $[I]_0/[C]_0$.

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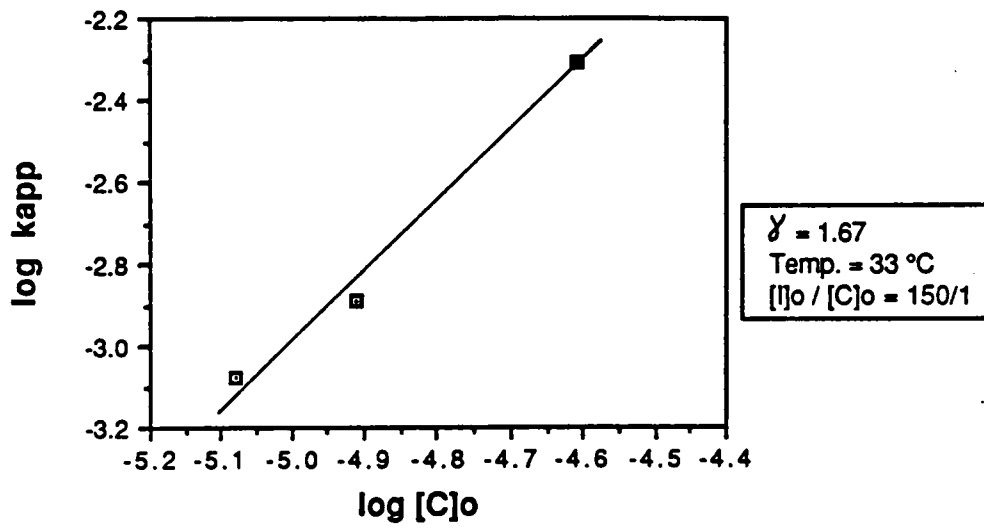


Figure 21. Bilogarithmic Plot of k_{app} vs Concentration of TBAB with a Constant Ratio of $[I]_o/[C]_o$

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first order dependence on the apparent rate of propagation in GTP with respect to TBAB concentration.

EFFECT OF TEMPERATURE ON THE POLYMERIZATION RATE. By varying the temperature of a chemical reaction one can elucidate information regarding the energy of activation under a certain set of reaction conditions. It must be kept in mind when considering a mechanism such as GTP, that a catalyst is required and, by its nature, serves to lower the energy of activation for the reaction without being permanently altered itself. Thus, experiments to elucidate the global E_a for GTP of MMA with TBAB and MTS were carried out with constant concentrations of reagents and a mole ratio of initiator to catalyst corresponding to 150/1. As described previously the first order time-conversion plots were constructed from which the apparent rate constants (k_{app}) were obtained (Figure 22). Subsequently, an Arrhenius plot for the polymerization rate constants was constructed (Figure 23).

As demonstrated by Mai and Müller using TASHF₂ as the selected catalyst, the linearity of the plot using TBAB renders evidence for the existence of only one active species [122]. The E_a determined from the slope of the Arrhenius plot (Equation 23) was +20.4 kJ/mole (Eq.23)

$$\log(k_p) = -(E_a/RT) + \log A \quad \text{Eq. 23}$$

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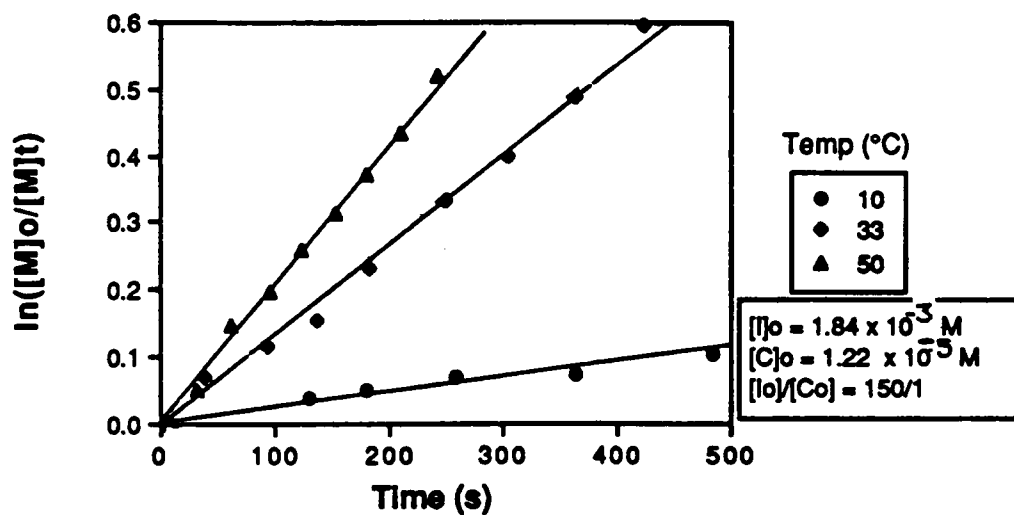


Figure 22. First Order Time Conversion Plots for Various Temperatures of Polymerization

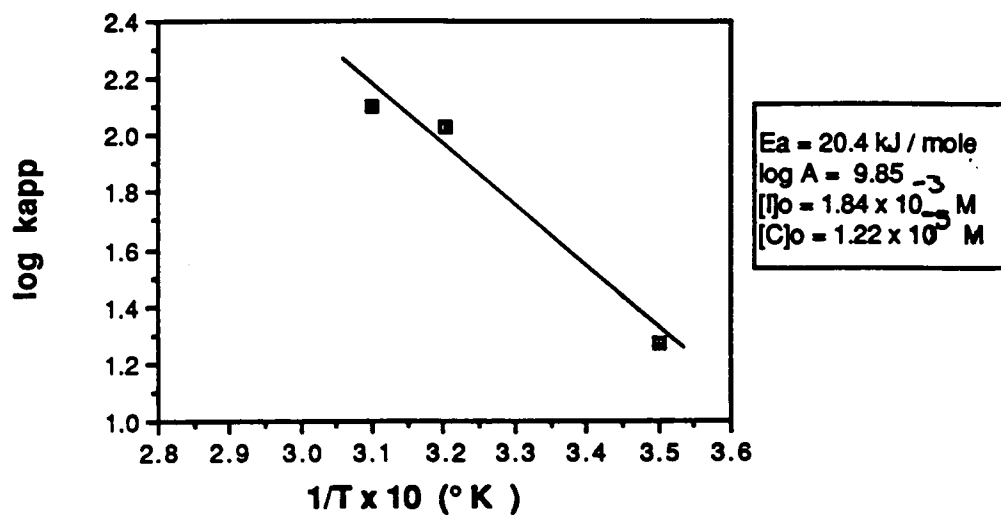


Figure 23. Arrhenius Plot

A value of 16.9 kJ/mole was reported by Mai and Müller using TASHF₂ as the selected catalyst [122]. Since TBAB is a weaker base, one would predict the global E_a for TBAB at a given concentration to be higher than that obtained for TASHF₂.

Müller also compares the E_a(TASHF₂) to the global E_a reported for the anionic polymerization of MMA using various counterions [122,124]. Based on the relative similarity of the E_a and stereochemistry between anionic (using a free anion, bulky, or strongly solvated counterion) to the reported GTP value using TASHF₂, Müller proposed a two step "associative" mechanism of monomer addition for GTP (Scheme 14). Though the value obtained for the global E_a using TBAB in our investigations is similar to that reported by Mai and Müller, a direct comparison to anionic and free radical mechanisms is difficult. In free radical and anionic mechanisms, variations in temperature and solvent may lower the E_a by causing the reaction to occur at a faster rate, however GTP is catalyzed. Unlike the potential effects of temperature and solvents, a catalyst does not operate by making the uncatalyzed reaction faster but introduces a different, more favorable pathway [200]. Thus, from this reasoning, it is difficult from the limited number of kinetic investigations conducted at this point to eliminate either the concerted associative mechanism, two-step "associative" mechanism or an alternative pathway.

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OTHER CONSIDERATIONS. A unique molecular weight distribution arises with some polymerization mechanisms in the absence of terminating side reactions and under the conditions of fast initiation relative to propagation. By its living nature, the active centers in GTP should grow at the same time and add monomer at equal rates. From kinetic arguments which invoke a constant concentration of active centers, $[P^*]$, (Eq.24)

$$-d[M]/dt = k_p \cdot [M] \cdot [P^*] \quad \text{Eq. 24}$$

the kinetic chain length, v , for GTP can also be described by Equation 25 [201].

$$v = \frac{[M]_0 - [M]}{[P^*]} - 1 = \langle i_n \rangle \approx \langle i_w \rangle \quad \text{Eq. 25}$$

It follows that the polymers should have molecular weight distributions which approximate the Poisson distribution.

The polydispersity for a Poisson MWD is found to be

$$\langle Mw \rangle / \langle Mn \rangle = 1 + (\langle i_n \rangle - 1) / \langle i_n \rangle^2 \approx 1 + (1 / \langle i_n \rangle) \quad \text{Eq. 26}$$

From the kinetic investigations, the molecular weight distribution can be followed as a function of conversion

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(Figure 24). Plotting the molecular weight distribution vs conversion, a relatively insignificant narrowing of the distribution is observed as the chain length increases with conversion. These results are consistent with the nature of living polymerizations, though deviation is observed in the molecular weight vs conversion plots (Figure 25). The deviation from linearity through zero on both axes has been attributed largely to the methods of sample analysis, NMR for the percent conversion and SEC or GPC for the $\langle M_w \rangle$ and $\langle M_n \rangle$. A method such as vapor phase osmometry, VPO, may permit a more accurate determination of the $\langle M_n \rangle$ than GPC for low molecular weight or low conversion samples. Though PMMA standards were employed for the calibration, at low conversions during any given kinetic run, sample analysis by GPC may have been beyond the column separation limits. Therefore, it is difficult to accurately compare the values of $\langle M_n \rangle$ and $\langle M_w \rangle$ obtained from this relative method to the conversion data.

SUMMARY. Table 25 summarizes the kinetic results obtained for the GTP of MMA using TBAB as the selected catalyst and a low pressure polymerization reactor. It is difficult to make any definitive statements regarding the kinetics of GTP from these initial studies. It does appear however that the kinetic expression may be more complex than that originally proposed and significantly dependent on the

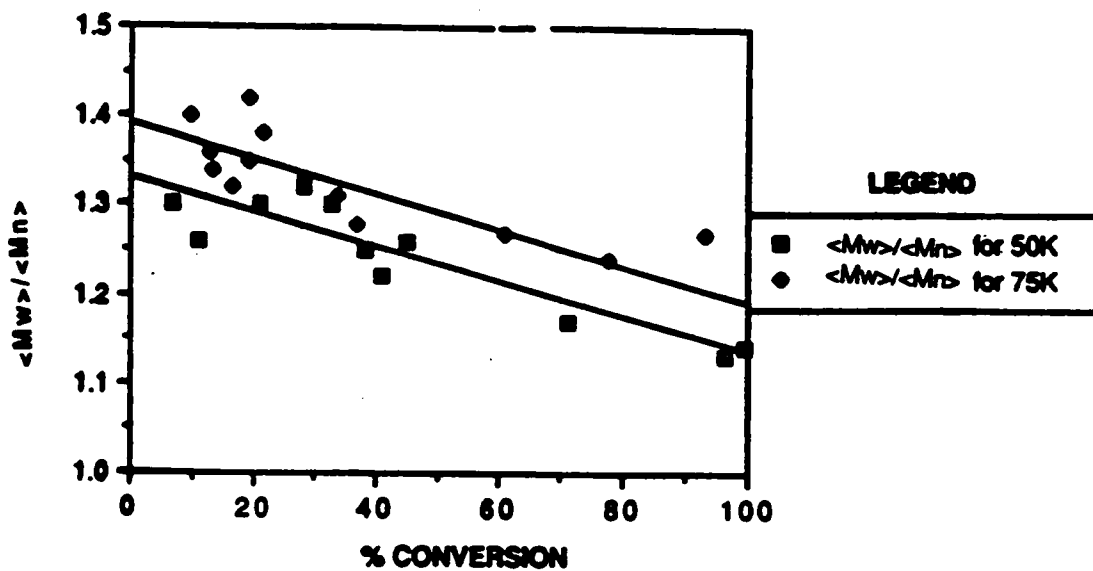


Figure 24. Molecular Weight Distribution vs
& Conversion

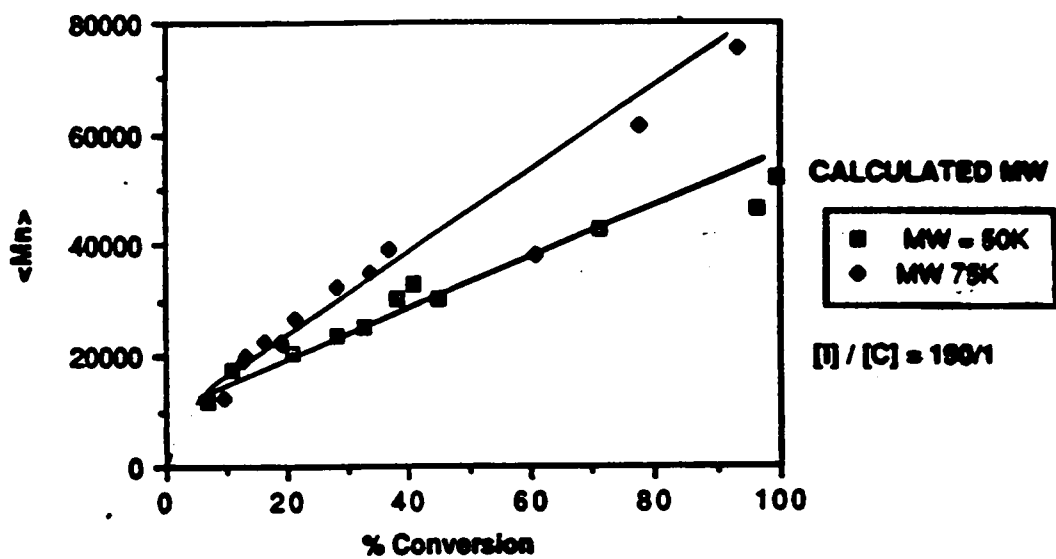


Figure 25. Molecular Weight vs % Conversion

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Table 24: Summary of Kinetic Results For the GTP of MMA using MTS and TBAB

Study	Variables	Constants	Reaction Order	Ea kJ/mole
1	$[C]_0, [I]_0/[C]_0$	$[I]_0, \text{Temp.}$	$r = 1.53$	--
2	$[I]_0, [I]_0/[C]_0$	$[C]_0, \text{Temp.}$	$\beta = -1.06$	--
3	$[I]_0, [C]_0$	$[I]_0/[C]_0, \text{Temp}$	$r = 1.67$ $\beta = 0.65$	-- --
4	Temp.	$[I]_0, [C]_0,$ $[I]_0/[C]_0$	-----	20.4

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level of catalyst. That is, at higher levels of catalyst, the rate determining step may be strictly the addition of monomer. At very low concentrations of catalyst one would predict that the decomposition rate of activated initiator or activated propagating chain end would be the rate determining step. However, at moderate catalyst levels and consequently, moderate $[I]_0/[C]_0$ mole ratios, both the decomposition and propagation step may become partially rate limiting (k_{-1} and $k_p[M]$ are comparable) and then the kinetic expression is more complex. This dependency on catalyst level is proposed here though more data is needed for further support. Again, it is difficult to compare the results of the limited number of kinetic investigations between investigators due to the variations in concentrations of reactants and products, mode of addition of reagents, physical conditions; pressure, temperature, and viscosity. However, with more systematic studies, bridges between the data may be formed and provide a basis for making comparisons and mechanistic deductions.

SYNTHESIS AND CHARACTERIZATION OF POLY(DIMETHYLSILOXANE) OLIGOMERS.

INTRODUCTION. Siloxane block and graft copolymers attract both industrial and academic attention because of

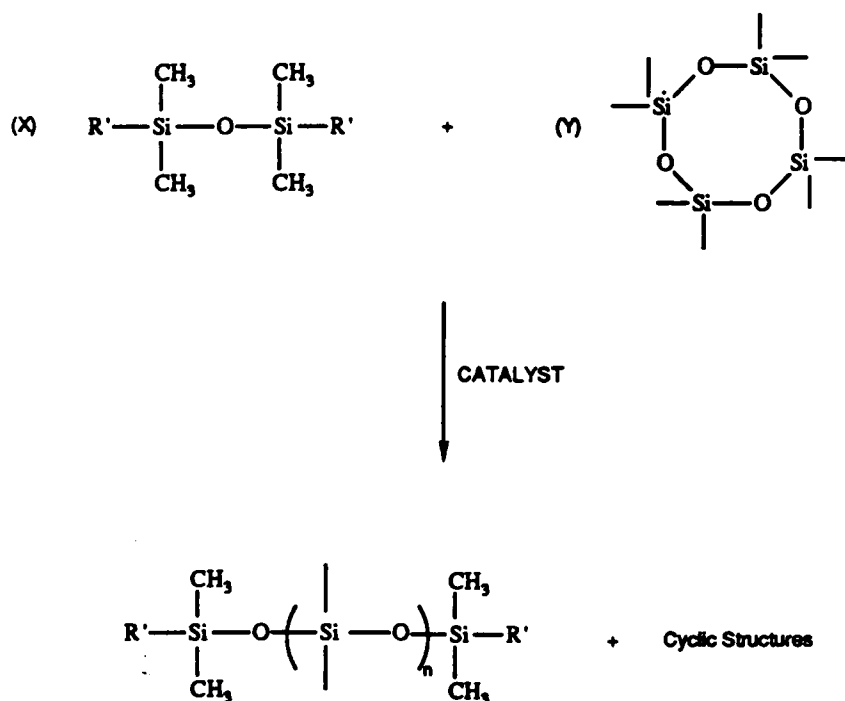
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the retention of the unique features imparted by the siloxane component both in the bulk and at the surfaces of heterophase polymeric materials [202-205]. Some of these characteristics are listed in Table 25. Reactions which follow various polymerization mechanisms have been employed to prepare the siloxane component for the preparation of multiphase polymer systems [191, 207-209]. For example, the ring opening polymerization of octamethylcyclotetrasiloxane (D_4) with a suitable catalyst, either acidic or basic, in the presence of an end-blocker provides for the preparation of a host of siloxane oligomers which can serve as suitable intermediates for segmented copolymers (Scheme 20) [191,204,206,209]. During the course of this mechanism an equilibrium mixture of cyclic and linear species is produced. In addition, the molecular weight is governed by the equilibria with the endblocking species. Using various endblocking reagents, such as amino propyl, carboxy propyl and epoxy propyl, a variety of oligomers have been prepared [206].

Contrary to typical anionic ring opening polymerizations where potassium silanolates are employed, little or no equilibration is observed with lithium as the counterion. Strained cyclic monomers, such as hexamethylcyclotrisiloxane (D_3), have been polymerized using a solvent promoted lithium silanolate initiator. Under suitable conditions of time and

TABLE 25: PROPERTIES OF SILOXANES

- * Low Temperature Flexability (low Tg)
- * Low Surface Free Energy
- * Excellent Electrical Properties
- * Ozone Resistance
- * Permeability Toward Gases
- * Biocompatibility
- * Thermal Stability
- * Transparent and Stable to UV



Scheme 20. General Schematic of the Ring Opening Polymerization of D_4

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temperature, the anionic ring opening polymerization mechanism proceeds without equilibration in a small amount of polar component (solvent or promoters), giving rise to the preparation of well defined living polymers of controlled molecular weight and narrow molecular weight distribution [36,204,210,211]. In addition, multiphase materials can be prepared by the appropriate choice of terminating agent or the sequential addition of a second polymerizable monomer [202,205,211-213].

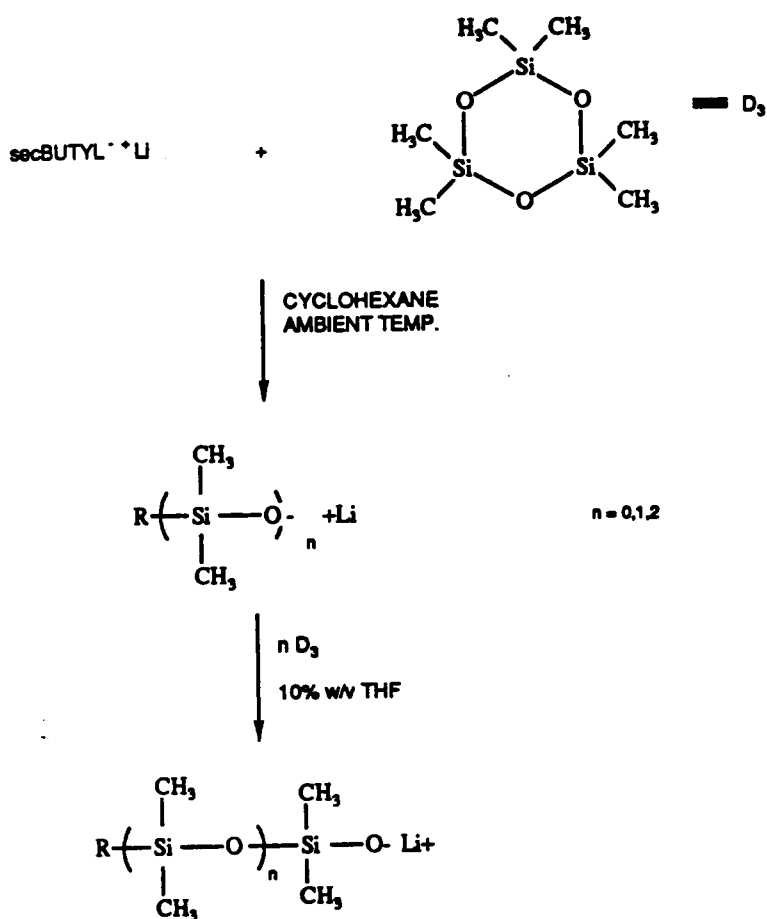
PDMS PRECURSORS FOR BLOCK & GRAFT COPOLYMERS. In this research, the key to the preparation of well defined multicomponent systems, using GTP as the second copolymerization mechanism, has been use of the anionic ring opening polymerization of D_3 with sec-butyllithium. This mechanism permits the preparation of functional poly(dimethylsiloxane) oligomers which were fully characterized with respect to molecular weight and functionality prior to either modification or copolymerization.

As described in the experimental section, the monomer, D_3 , was purified by sublimation and stored in solution in purified cyclohexane. In addition to its hydrophobic character and absence of side reactions over long storage periods, cyclohexane was conveniently chosen as the polymerization solvent particularly with the selected initiator, sec- butyllithium. Under selected conditions,

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anionic initiators possessing lithium as the counterion are highly associated. In cyclohexane, sec-butyllithium initiates the polymerization of D_3 ; however, the tight ion pair formed in this nonpolar solvent is incapable of propagating the polymerization. This forces rapid initiation, relative to propagation, by permitting complete initiation so that all chains will appear to eventually propagate at the same time preserving the living nature of the polymerization. The nature of the lithium silanolate species in this nonpolar environment is not entirely clear. Frye et al. [210], reported the formation of $R-Si(CH_3)_2-O^- Li^+$ as the primary structure obtained in hydrocarbon solvents as depicted in Scheme 23. More recently, Riffle et al. [211], have elucidated the existence of a number of species using ^{29}Si NMR which render support for the aforementioned structure. By the addition of a polar aprotic solvent, such as THF (10 % w/vol), propagation occurs with the solvent promoted lithium silanolate species (Scheme 23).

In order to prepare precursors for subsequent copolymerization, the living siloxane polymers were terminated with an appropriate reagent. A number of functionalized poly(dimethylsiloxane) homopolymers were prepared throughout this research. The methacryloxy functionalized oligomers were used most extensively for further copolymerization by GTP. The propagating lithium



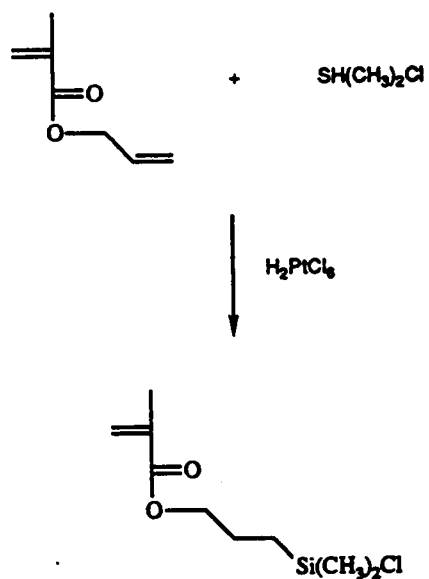
Scheme 21. General Schematic of the Anionic Ring Opening Polymerization of D_3

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silanolate was terminated with a chlorosilane derivative of allyl methacrylate, 3-methacryloxypropyldimethylchlorosilane [167,168,172]. At times this reagent was not readily available from Petrach Chemical and was consequently prepared.

This reagent is an adduct prepared by the hydrosilylation of allyl methacrylate and chlorodimethylsilane in the presence of chloroplatinic acid as depicted in Scheme 24 and described in the experimental section, [167-168]. J.L. Speier [214] has extensively reviewed the diversity of soluble complexes of transition metals, like chloroplatinic acid, for the hydrosilylation of substituted and unsubstituted unsaturated hydrocarbons. As a homogeneous catalyst for hydrosilylation of unsaturated compounds, such as allyl methacrylate, an unpredictable exothermic induction period is observed with chloroplatinic acid. Throughout the synthesis, it is important to maintain a reaction temperature less than 70 °C to prevent the decomposition of the catalyst. A further complication during our hydrosilylation reaction was prevention of the thermal polymerization of allyl methacrylate. During this inductive period the active catalytic species is formed which requires the reduction of chloroplatinic acid. Speier [214] has reported that no direct proof exists for the structure of the active catalytic species during hydrosilylation, though evidence does indicate that the

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Scheme 23. Synthesis of 3-Methacryloxypropyldimethylchlorosilane

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mechanism of hydrosilylation takes place within the coordination sphere of the transition metal. The hydrosilylation reaction producing the chlorosilane derivative of allyl methacrylate was monitored by IR and NMR. The consumption of chlorodimethylsilane was monitored by observing the disappearance of the Si-H stretching band (2170 cm^{-1}), permitting the aliquot addition of this reagent while preventing an undesirable temperature increase ($\geq 70\text{ }^{\circ}\text{C}$). Figure 26 illustrates the formation of the terminating agent as followed by NMR. The catalytic activity of chloroplatinic acid was also useful for the hydrosilylation reaction of vinylbenzylchloride, which when used as a terminating agent yields a benzylchloride functionalized siloxane oligomer. Table 26 lists some of the useful IR bands and NMR chemical shifts for the formation of these two reagents.

As terminating reagents to produce functionalized siloxane oligomers, these reagents were charged directly to the living siloxane under inert conditions. Precipitation of lithium chloride, as a by-product, was a useful indicator of the termination reaction, and was also a driving force for the formation of the functionalized oligomer. After the described work up, the functionalized oligomers were characterized extensively by a variety of techniques which include GPC, VPO, UV spectroscopy, and NMR (Table 27).

The calculated molecular weight of the siloxane

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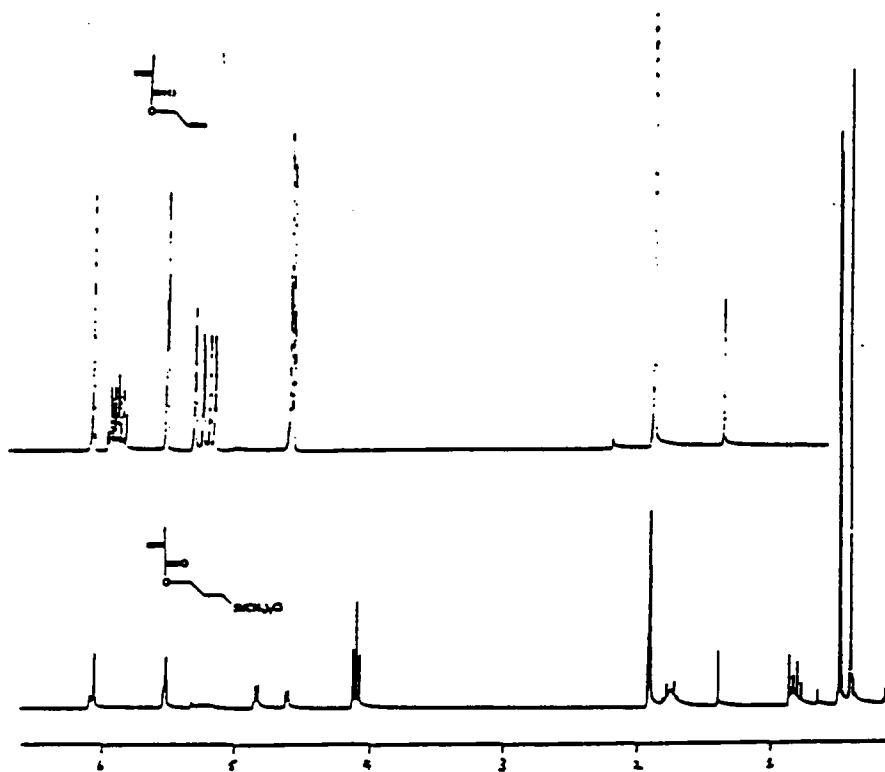
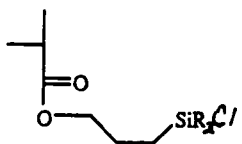
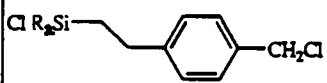


Figure 26. ^1H NMR of the formation of 3-Methacryloxypropyl dimethylchlorosilane

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TABLE 26: SPECTRAL DATA FOR SILOXANE TERMINATING AGENTS

Structure	NMR ($-\delta$ ppm)	IR (cm^{-1})
	A) 5.8, 6.4 B) 4.4 C) 2. D) 1.9 E) 0.	Si-H 2170 (disappearance)
	A) 7.5 B) 4.8 C) 4.6 D) 0.1	

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TABLE 27: CHARACTERIZATION OF POLY(DIMETHYLSILOXANE) OLIGOMERS

PDMS MW ^a	VPO ^b	UV ^c	¹ HNMR ^d	GPC ^e	
				<Mn>	<Mw>/<Mn>
1,000	1,600	2,000	1,950	---	----
5,000	5,600	4,700	-----	7,500	1.15
10,000	9,800	8,800	-----	14,000	1.10
20,000	-----	30,000	-----	27,000	1.20

^a Calculated Molecular Weight

^b Toluene at 63 °C

^c max = 214 nm, MMA standard, cyclohexane

^d Based on PS stds.

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oligomers covered a range of 1000 (1k), to 20,000 (20k). The number average molecular weight and molecular weight distribution of each oligomer was determined using GPC as a primary method. The presence of the methacryloxy or in some cases benzylchloride moiety on the chain end permits the use of a UV detector for an otherwise UV transparent material. Use of this detector to analyze the functionalized polymer is also necessary when the mobile phase for the analysis is THF. Due to the similarity in refractive indices of solvent and siloxane oligomer, a refractive index detector for analysis is not useful in THF. The siloxane oligomers were detected by refractive index using a smaller column set in the chromatograph and toluene as the transport solvent. When the average molecular weight of the siloxane oligomer was $\leq 1k$, the use of the a column set having one column of a porosity of 100 \AA , the oligomer was efficiently fractionated in toluene which prevented the determination of the molecular weight and molecular weight distribution. The molecular weights and molecular weight distributions were determined with respect to either poly(styrene) or poly(dimethylsiloxane) standards. As seen from Figure 27 and Table 27, the preparation of relatively narrow molecular weight distribution PDMS oligomers was successfully achieved. Table 27 also summarizes the characterization and degree of control for the polymerization of a variety of

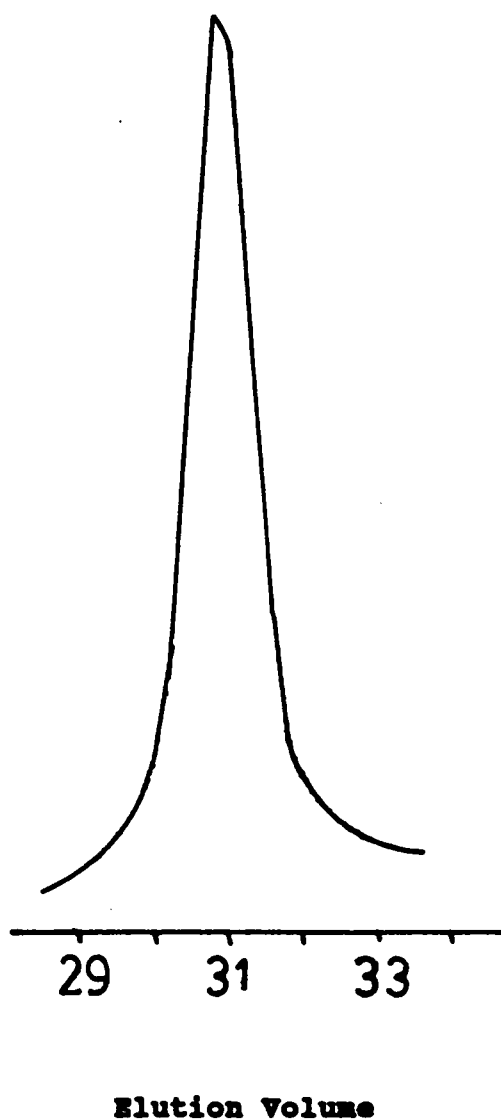


Figure 27. GPC Trace of Poly(dimethylsiloxane) Oligomer Prepared by Anionic Ring Opening Polymerization

molecular weight poly(dimethylsiloxane)s by the anionic ring opening polymerization of D_3 . Other analytical techniques were used during characterization in order to confirm the molecular weight determined by GPC and gain insight into the functionality of these oligomers. As described in the experimental chapter, due to the absorbance of the methacrylate moiety at 218nm, UV spectroscopy was conveniently used to determine molecular weight through end group analysis. In addition, vapor phase osmometry (VPO) provided further agreement (within experimental error) for molecular weight determination between the various characterization tools. It must be recognized that an upper limit of ca. 30,000 g/mol exists for the determination of molecular weight by VPO. Similarly, 1H NMR can be used for molecular weight determination by integration, though, an upper limit exists depending upon the field strength of the instrument (ca. 3,000 g/mol). For the 1k PDMS oligomers, molecular weight was determined using NMR by the ratio of the integration of the methoxy proton signal of the end group (4.5 ppm) with respect to the integration of the methyl proton signal of the siloxane repeat unit (0.3 ppm) (Figure 28).

The characterization of the PDMS oligomer molecular weights can be easily achieved by a variety of analytical means, but the quantitative efficiency of functionalization is a continuing issue in the preparation of functional

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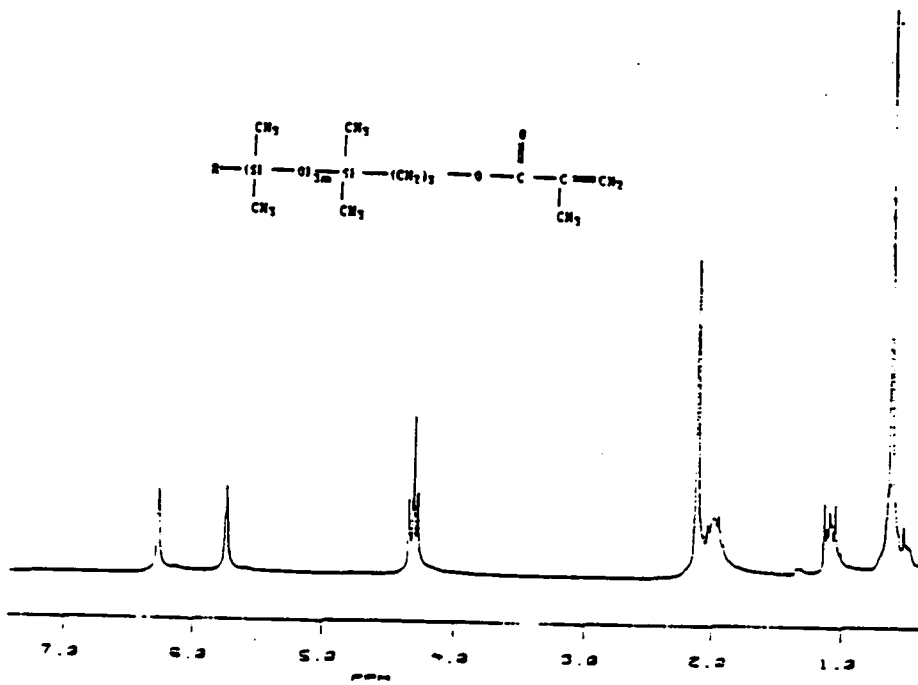


Figure 28. ¹H NMR of Methacryloxy Functionalized Poly(dimethylsiloxane) Oligomer

materials prepared by living polymerization methods [215]. The premature termination of the propagating chain ends by impurities is one source of homopolymer contamination, as well as loss in composition control, when these functional materials are utilized in subsequent postreactions.

Recently, with the advent of pulsed Fourier transform spectrometry, computer signal averaging, and relaxation reagents, facile NMR studies on nuclei of low natural abundance have been possible [188,216-219]. Despite the preexisting problems of low natural abundance (4.7%), relatively long relaxation times ($T_1 > 20$ sec), low signal sensitivity (0.008 relative to $^1\text{H} = 1.0$) and the negative nuclear Overhauser effect ($\text{NOE} = -0.555$) that are characteristic of the magnetically active silicon isotope, ^{29}Si FTNMR has been successfully utilized for the characterization of silicon containing materials [216,218] and extensive compilations of chemical shift data are available [216-218].

The utility of silicon 29 NMR, as used in this research, was to determine the functionality of the siloxane oligomers. Since in ^{29}Si NMR, the silicon chemical shift changes with respect to its substituents, functionality and molecular weight were easily determined. For the methacryloxy terminated PDMS oligomers the percent functionality was determined by the ratio of the integration of the signal due to the silicon adjacent to the

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methacryloxy fragment (7.36 ppm) with respect to the integration of the signal resulting from the silicon adjacent to the initiator fragment (8.6 ppm) (Figure 29 & Table 28). The anionic polymerization was initiated with sec-butyllithium, thus, it was assumed that each chain end has a sec-butyl group. There was no indication in the ^{29}Si NMR spectra of D_3 initiation by alkoxides. To confirm signal assignments, a variety of functionalized siloxane oligomers were prepared and characterized by ^{29}Si NMR (Table 29). As illustrated in Table 28 ratio of the integration of the initiating fragment signal relative to the integration resulting from the backbone silicon atoms, molecular weight can be determined. This technique, of course, becomes less sensitive for the determination of functionality and molecular weight as molecular weight is increased.

As mentioned previously, PDMS as one of the components of block and graft copolymers have been attracting interest due to their unique bulk and surface properties. In addition, incorporation of precisely defined oligomers of controlled molecular weight and narrow molecular weight distribution such as those described above, may elucidate structure-property information arising from microphase separated morphology of incompatible polymer components in various copolymer architectures.

It was a primary objective of this research to further utilize these PDMS oligomers, in conjunction with

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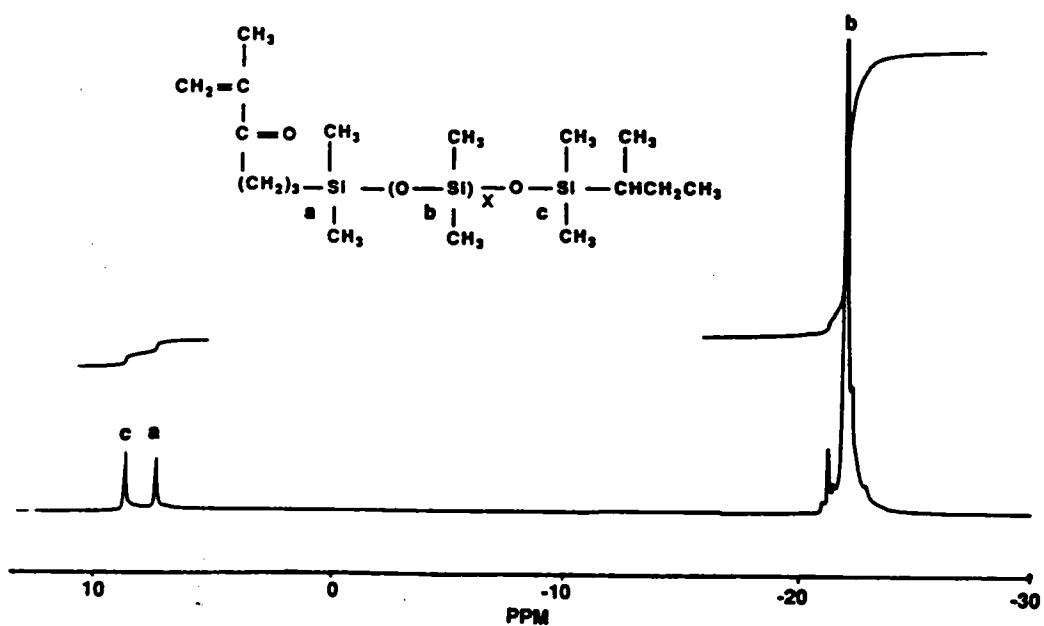


Figure 29. ^{29}Si NMR of Methacryloxy Functionalized Poly(dimethylsiloxane) Oligomer

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TABLE 28: DETERMINATION OF POLY(DIMETHYLSILOXANE) MACROMER^R FUNCTIONALITY

Molecular Weight (calculated)	% Functionality ^a	<Mn> ^a
1,000	93	1,670
5,000	95	8,880
10,000	89	12,000

^a ²⁹Si NMR (39.763 MHz) in CDCL₃ with 0.04M Cr(acac)₃

TABLE 29: CHEMICAL SHIFT OF PDMS SILICON ATOM
ADJACENT TO SELECTED FUNCTIONAL END GROUPS

Functional group	Chemical shift in ^{29}Si NMR δ (ppm)
<i>s</i> -Butyl-Si(CH ₃) ₂ O-	8.7
<i>t</i> -Butyl-O-Si(CH ₃) ₂ O-	-19.1
(CH ₃) ₂ -Ph-Si(CH ₃) ₂ O-	- 2.6
CH ₂ =CH(CH ₃)COO(CH ₂) ₃ -Si(CH ₃) ₂ O-	7.3
CH ₂ =CH(CH ₂) ₄ -Si(CH ₃) ₂ O-	7.5

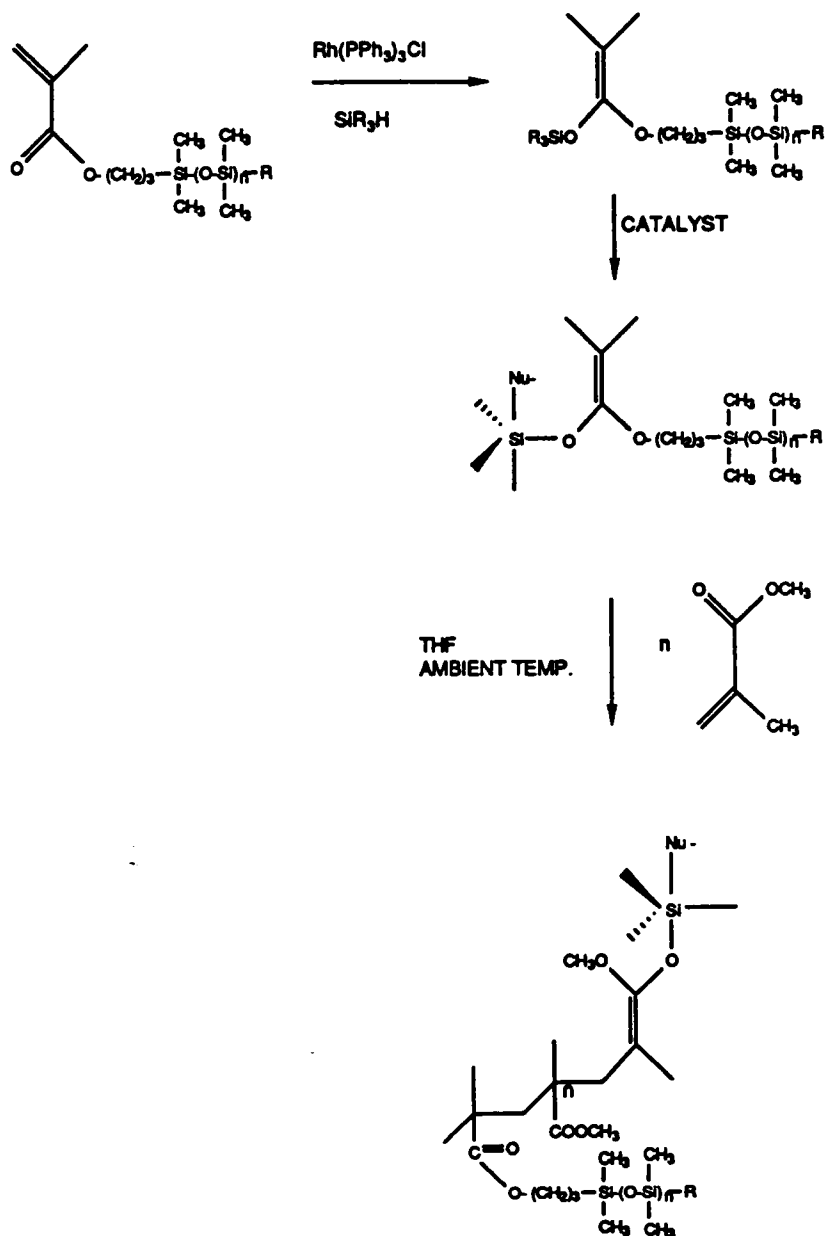
GTP, for the preparation of well defined block and graft copolymers. The preparation of poly(methyl methacrylate)-b-poly (dimethylsiloxane) copolymers will be addressed, followed by a discussion of the preparation of graft copolymers via the Macromer^R technique.

COPOLYMERS OF POLY(DIMETHYLSILOXANE)-B-POLY(METHYL METHACRYLATE)

INTRODUCTION. The impact of multiphase polymeric materials has been enhanced by the preparation of well defined block copolymers [133]. Hence, there has been a growing emphasis on new synthetic methods for the preparation of block copolymers. The evolution of transformation reactions, which were addressed briefly in the literature review, to interrelate different synthetic routes further extends the range of block copolymers which can be prepared, and therefore, the availability of well defined multiphase polymeric materials.

Group transfer polymerization, in combination with free radical techniques, has been used as one of the modes of polymerization in a transformation reaction to incorporate α, β unsaturated monomers into copolymers of controlled architecture [153]. The central point of discussion in this section will be the preparation of block copolymers via transformation synthesis from an anionic ring opening mechanism to GTP (Scheme 24). This will be addressed in

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Scheme 24. Transformation Synthesis from Anionic Ring Opening to GTP Mechanism

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detail following a brief review of some of the synthetic pathways that have previously been applied to prepare copolymers with methacrylic ester and siloxane monomers.

Though a variety of synthetic routes have been used to prepare graft copolymers of PMMA and PDMS, less work has been done preparing copolymers. To prepare PDMS-*b*-PMMA copolymers via sequential addition techniques, a limitation arises due to the insufficient basicity of the "living" silanolate to initiate the polymerization of vinyl monomers [133]. It has also been referenced that the anionic polymerization of the methacrylic monomer, followed by the addition of the cyclic siloxane monomer, yields the incorporation of only small amounts of the siloxane moiety in the copolymer [212]. In order to enhance the incorporation of the siloxane component in methacrylic ester-siloxane copolymers a number of investigators have utilized some interesting synthetic tools and each of the more recent methodologies will be briefly addressed.

LIVING POLYMERIZATIONS. In order to enhance the incorporation of the siloxane component and maintain the molecular weight control obtainable by anionic polymerization mechanisms, Juliano [220], and later Varshney [212], reported the preparation of PDMS-PMMA block copolymers using a difunctional initiator having sites of unequal reactivity. The initiator, having a hindered 1,1

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diphenylmethyl carbanion and an alkoxy anion, was a dilithiobenzophenone dianion. Though the initial intention was to selectively initiate D_3 with the alkoxy anion followed by the initiation of the alkyl methacrylate with the hindered carbanion, the presence of homopolymer PDMS indicates that D_3 may be initiated from both sites.

USE OF FREE RADICAL MECHANISM. Extending beyond the high vacuum techniques of Varshney et al., block copolymers containing PDMS and various alkyl methacrylates have been prepared via coupling reactions. In order to elucidate the interactions between blood platelets and polymer surfaces, Shimada et al., [221] prepared triblocks of poly(2-hydroxyethyl methacrylate) and PDMS by coupling isocyanate terminated difunctional PDMS oligomers (MW = 2,400) with free radically polymerized monofunctional amine terminated methacrylic ester oligomers (MW = 2,700-12,000). Though they were able to efficiently remove unincorporated oligomers resulting from both monomers, the yield of copolymer centered at ca. 30%. Due to the low efficiency of the coupling reaction of these low molecular weight oligomers if one were to replace the PHEMA component with PMMA the ability to remove the PMMA homopolymer contamination arises.

More recently Pietrasanta et al. [222] prepared PMMA-PDMS block oligomers which could serve as model compounds

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for the preparation of PMMA-PDMS triblock or graft copolymers. Their method of triblock formation involved reacting a mercaptopropylmethyldimethoxysilane functionalized PMMA oligomer with a hydroxyl functionalized PDMS homopolymer in the presence of 2-ethylhexanoic acid on tetramethylguanidine. Taking advantage of the high chain transfer abilities of thiol compounds (as did Shimada [221]) in free radical polymerizations, Pietrasanta [222] presented a novel route to the preparation of siloxane terminated PMMA. Though it was stated that the thiol concentration predicted the chain length ($DP = 1,2$) the possibility of preparing nonfunctional PMMA is still present. In the preparation of triblock materials where the degree of polymerization of the PMMA component is much larger than two, removal of homopolymer PMMA again does exist. As in the preparation of copolymers of siloxane and vinyl monomers using a PDMS macroinitiator described by Crivello et al. [208], this mechanism is dependent on control of free radical chain transfer processes and the mode of termination, combination vs disproportionation.

TRANSFORMATION SYNTHESIS. To circumvent the problem of PMMA homopolymer contamination within the block copolymer structure and maintain the attributes of living polymerizations, molecular weight control and narrow polydispersity, PDMS-b-PMMA copolymers were prepared via

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transformation synthesis involving anionic and GTP mechanisms (Scheme 24). Unlike the polymerization of this system using the difunctional anion, the copolymers were not prepared under the tedious reaction conditions required by high vacuum techniques. By the nature of transformation reactions, this synthetic tool permits the complete characterization of the first block and the functional end group which is to serve as an initiator for the second block.

For the formation of PDMS-*b*-PMMA, the PDMS first block was polymerized via the anionic ring opening polymerization of D_3 and capped with a chlorosilane derivative of allyl methacrylate. The synthetic procedure and characterization of these materials was discussed earlier. To polymerize the second monomer, MMA, via GTP, the methacryloxy functional end group of the siloxane oligomer was transformed into a ketene silyl acetal (Scheme 24). The selective and quantitative derivatization of the methacryloxy functional group in this reaction system is required primarily for two reasons; the inherent difficulty in the separation of the derivatized polymer from side products and starting materials, and the ability of methacryloxy terminal group to copolymerize with MMA under GTP conditions giving rise to a graft copolymer, thus contaminating the pure block copolymer architecture.

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this research, via transformation synthesis involving anionic and GTP mechanisms (Scheme 24). Unlike the polymerization of this system using the difunctional anion, the copolymers were not prepared under the tedious reaction conditions required by high vacuum techniques. By the nature of transformation reactions, this synthetic tool permits the complete characterization of the first block and the functional end group which is to serve as an initiator for the second block.

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α, β -Unsaturated esters have been shown to form ketene silyl acetals in very high yield via hydrosilylation reactions in the presence of a rhodium transition metal catalyst [71,72]. The conditions which would be necessary to quantitatively form the PDMS macroinitiating species in the presence of Wilkinson's catalyst were established using methyl methacrylate as a model compound. Also, to confirm that the catalyst did not degrade the polymer backbone, a PDMS oligomer was reacted with the rhodium catalyst. No change in the molecular weight or molecular weight distribution was observed as determined from GPC.

Confirmation of the quantitative hydrosilylation of the PDMS chain end was determined by proton NMR and FTIR. As the hydrosilylation reaction proceeds, the disappearance of the vinylic protons (5.5, 6.1 ppm) and α -methyl protons (2.2 ppm) of the methacryloxy group was observed with time (Figure 30). The protons of the two β -methyl groups of the ketene silyl acetal were observed to increase as the reaction proceeds. As spectra were collected, a shift in the triplet of the methylenic ester protons centered at 4.1 ppm to a triplet centered at 3.7 ppm was observed. A triplet centered at 4.0 ppm was sometimes observed and was attributed to result from the hydrolysis of the ketene silyl acetal moiety. This may have resulted from reaction of the end group with moisture or more likely reaction with residual methanol used to isolate the siloxane oligomer. In

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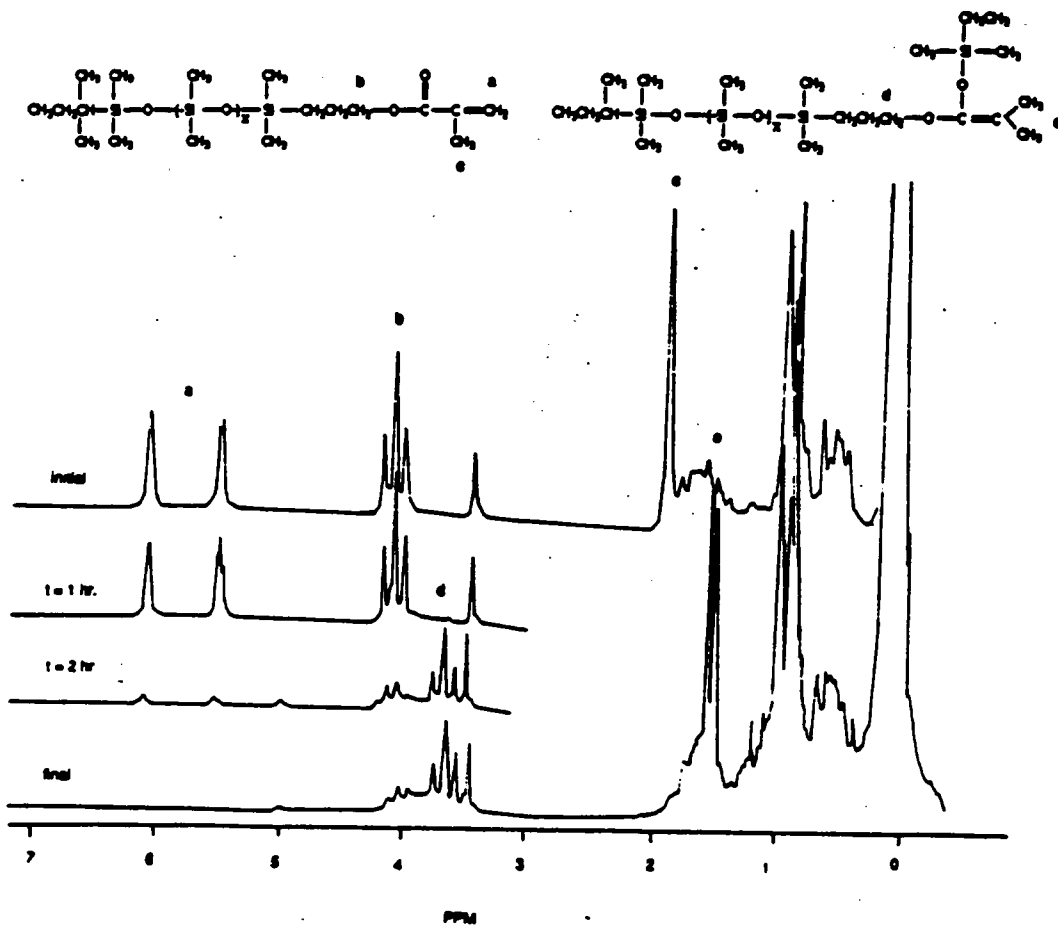


Figure 30. ^1H NMR of PDMS Macroinitiator Formation

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order to circumvent this problem, subsequent oligomers were isolated by filtration through a column of dry Celite^R under nitrogen to remove the termination by-product, lithium chloride, followed by removal of the solvent, cyclohexane, by vacuum stripping. In situations where methanol was used in the isolation procedure, it was determined that finely ground calcium chloride sufficiently removed residual methanol as determined by proton NMR [223].

To minimize exposure of the methacryloxy PDMS oligomer to protic sources, formation of the ketene silyl acetal macroinitiator, and the subsequent GTP of MMA was carried out in the presence of the lithium chloride salts. Complete conversion of MMA was not obtained as indicated by the strong odor of MMA. Isolation of the copolymer from unincorporated PDMS homopolymer to determine the composition was not possible due to the viscous nature of the material.

Focusing again on the PDMS macroinitiator, further characterization involved FTIR. As the isolated methacrylate functionalized PDMS oligomer was derivatized, a shift in the carbonyl band (1725 cm^{-1}) was observed upon O-silylation of the carbonyl oxygen (1705 cm^{-1}) (Figure 31). The carbonyl band observed at 1738 cm^{-1} corresponds to hydrolyzed product. It is assumed that the macroinitiator hydrolyzed during accumulation of the IR spectra, though this is difficult to quantify. ^{29}Si NMR was also used to observe the formation of the ketene silyl acetal

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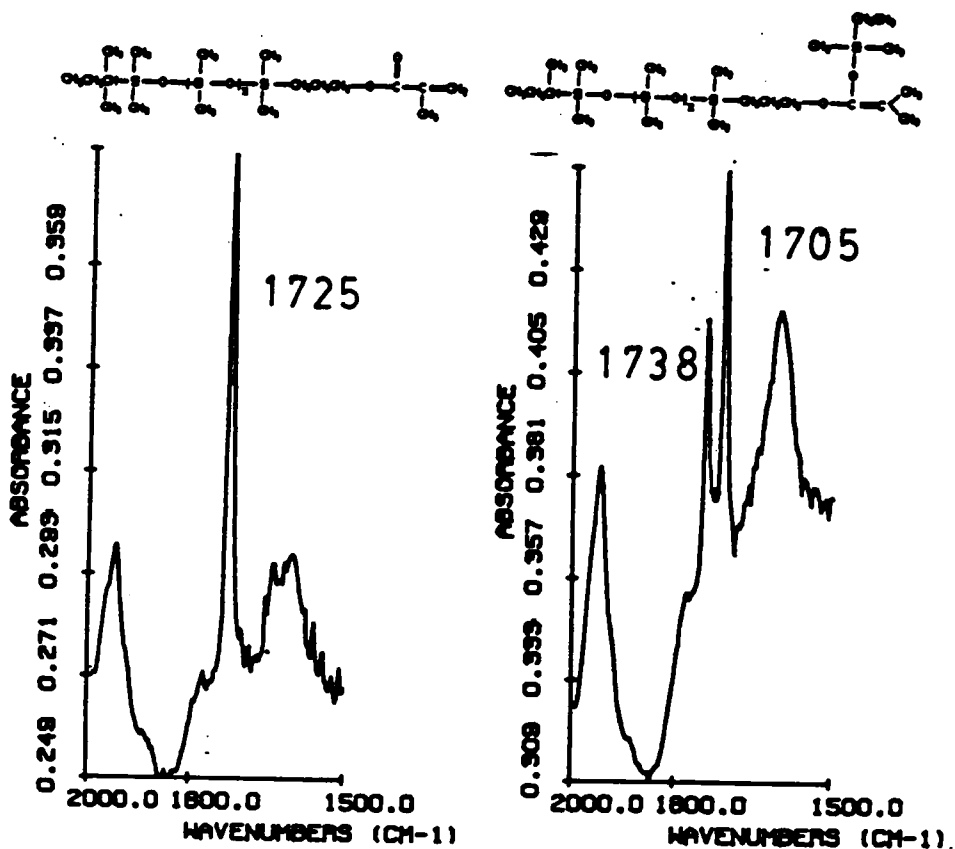


Figure 31. FTIR of PDMS Macroinitiator Formation

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macroinitiator and to determine the efficiency of the reaction. The efficiency of the reaction could be directly determined by ratioing the integration of the signal of the silicon atom of the ketene silyl acetal group (21.1 ppm) relative to the signal from the silicon atom adjacent to the methacryloxy group (7.36 ppm) (Figure 32).

The quantitative formation of the macroinitiator, as confirmed by NMR and FTIR, is quite encouraging for the efficient GTP of MMA. The reaction conditions necessary for the controlled polymerization of alkyl methacrylates by GTP were addressed in detail in the first section of this chapter. It was illustrated there and documented in the literature [66,67,77], that a variety of nucleophiles could serve as efficient GTP catalysts. The selection of the catalyst becomes more critical in the preparation of block and graft copolymers using the GTP mechanism in which PDMS is a component of the multiphase system. Using GPC, it was demonstrated that not all GTP nucleophilic catalysts are useful. Methacryloxy functionalized PDMS oligomers were mixed with various GTP catalysts in THF. As illustrated in Figure 33, no apparent change in molecular weight or molecular weight distribution was observed for the oligomers reacted with the acetate or benzoate based catalysts. From the GPC trace of the oligomer with tetrabutylammonium fluoride, it is apparent that the fluoride catalyst reacted with the PDMS oligomer causing the formation of the cyclic.

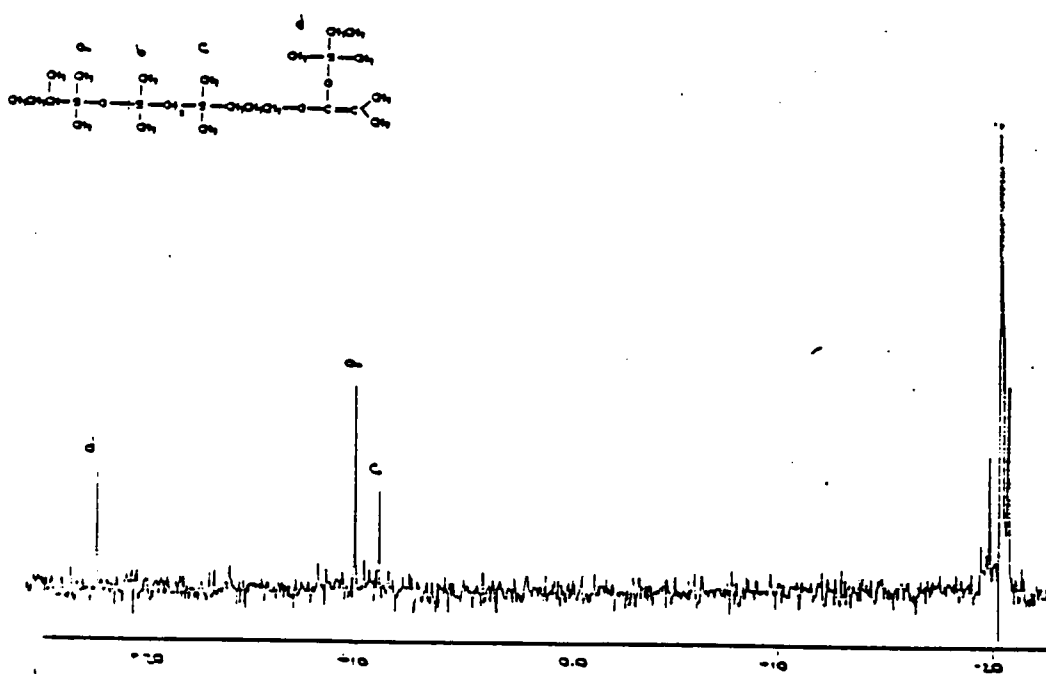


Figure 32. ^{29}Si NMR of PDMS Macroinitiator Formation

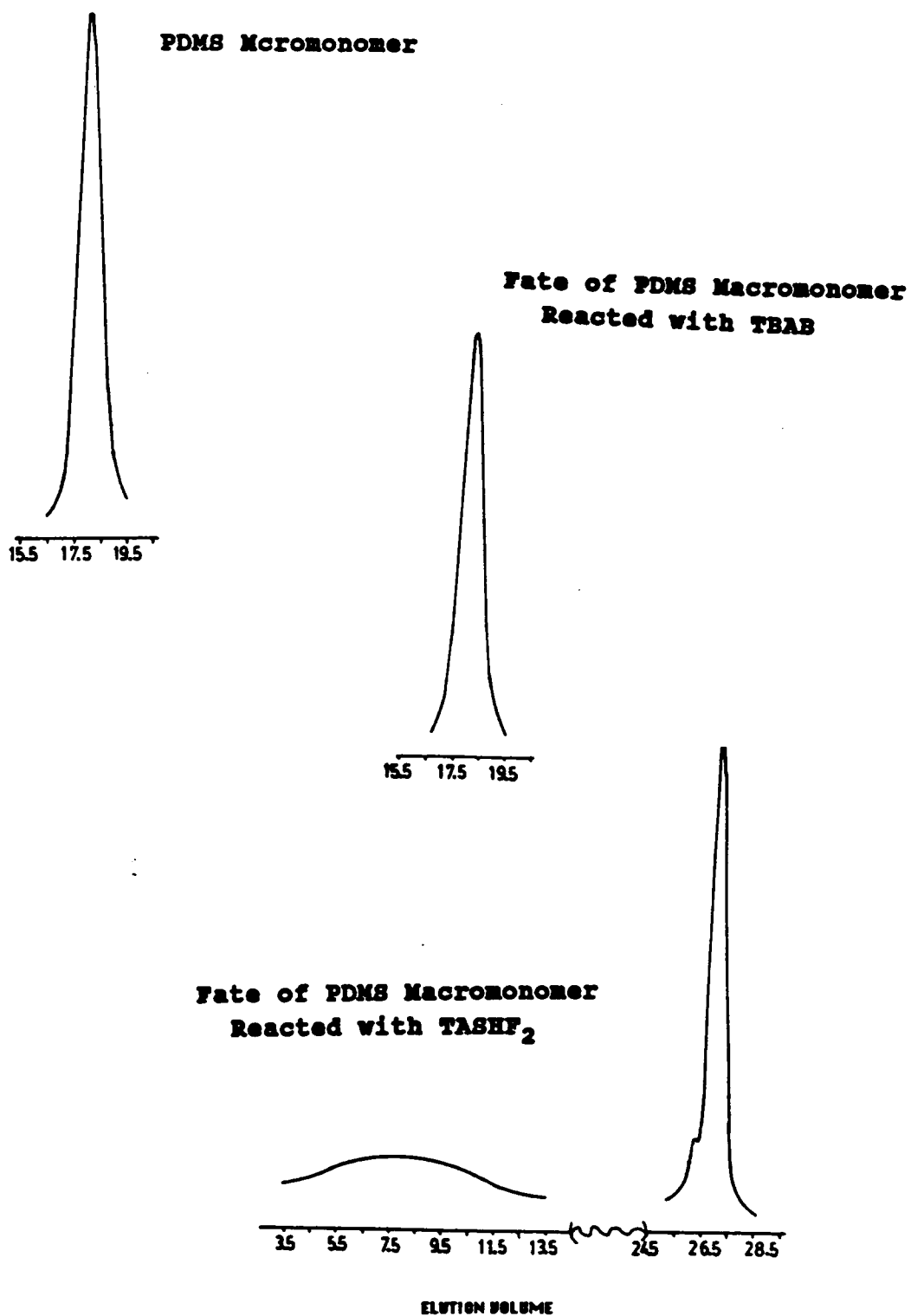


Figure 33. GPC Trace of Poly(dimethylsiloxane) Oligomers After Reaction with Various GTP Catalysts

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D₄ and oligomers yielding a Gaussian distribution. Hence, it was determined that fluoride based catalysts were unacceptable for the GTP of MMA with PDMS as the other block or graft component.

The GTP of MMA with the PDMS macroinitiator was carried out at ambient temperatures in the presence of tetrabutylammonium benzoate. It was not possible to isolate the PDMS macroinitiator from the rhodium catalyst prior to the GTP of MMA, however the excess silane from the hydrosilylation reaction was vacuum stripped from the reaction vessel. It was necessary to remove the residual silane to prevent the formation of ketene silyl acetal from MMA in the presence of Wilkinson's catalyst. After restoring a nitrogen atmosphere, the polymerization solvent, THF, was charged followed by the addition of the catalyst. The macroinitiator and catalyst were permitted to complex (5-10 min.) prior to addition of the monomer forming the proposed pentacoordinate silicon intermediate which represents the active initiating species. The polymers were isolated by precipitation into methanol and filtered. Unincorporated PDMS oligomers were removed from the block copolymer by extraction with hexanes in a soxhlet extractor.

Proton NMR confirmed the presence of PDMS in the block copolymer. The wt % PDMS incorporated was less than theoretically calculated (Table 30). The efficiency of the

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TABLE 30: WEIGHT % PDMS INCORPORATED INTO PDMS-b-PMMA COPOLYMERS

MW PDMS	Wt % PDMS Charged	WT% PDMS ^a Before Extraction	WT% PDMS ^a After Extraction
1,000	7.5	6.5	1.5
20,000	20.0	19.5	7.1
20,000	17.0	----	7.0
20,000	33.0	32.0	10.0

^a Determined by ¹H NMR (270 MHz) in CDCl₃

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transformation from anionic to GTP based on the apparent initiator efficiency (Eq. 27) ranged from 20-30%, which is

$$\frac{(\text{Yield}) \times (\text{PDMS in block copolymer})}{\text{PDMS in feed}} = \text{Apparent initiator efficiency} \quad \text{Eq. 27}$$

higher than reported for other transformation reactions. A plausible explanation for the poor efficiency may be loss of initiator efficiency. ^1H NMR analysis of the material recovered after extraction was confirmed to be hydrolyzed PDMS oligomer. There was no indication that block copolymer fractions high in PDMS were extracted. However, it is interesting to note that the apparent molecular weight distribution of the copolymers were broader than expected. Comparing the GPC trace of a siloxane oligomer and GTP-PMMA homopolymer with respect to a PDMS-PMMA block copolymer illustrates this point more clearly. Though substantial exotherms of polymerization are readily detected for GTP homopolymerizations, for block copolymers only small exotherms (≤ 5 °C) were detected over long time periods (1 hr.). This may be an indication that impurities are interfering or it may be speculated that a mechanistic limitation is present. Since the mechanism of GTP involves complexation of the nucleophilic catalyst to the silicon atom of the initiator, it is proposed that the catalyst may also complex to silicon atoms of the siloxane oligomer. Since the number of PDMS oligomer silicon atoms greatly

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exceeds the number of initiating fragment silicon atoms the probability of complexation to the oligomer is high. This would result in a slower rate of initiation and propagation because the relative amount of catalyst available to form the active pentacoordinate species necessary for propagation would be reduced. One could also speculate that fluctuation in the relative amount of catalyst available for GTP may arise at any given time depending on the type of silicon atom the catalyst complexes with. This topic will be addressed further in the discussion of the results of the PMMA-g-PDMS copolymers in which GTP was used to copolymerize MMA and PDMS macromonomers.

In spite of the nonideal efficiency of the transformation data, this method permits the preparation of PDMS-b-PMMA copolymers having theoretically no PMMA and PDMS homopolymer contamination. Further characterization of the copolymer having 10 wt% PDMS involved DMTA (Figure 34). As indicated from the elevation of the low temperature T_g (-112.5°C) of the PDMS component some phase mixing is evident in this copolymer. Since there is no depression of the high T_g , it could be speculated that most of the hard phase, on a weight basis, is unmixed. In the absence of DMTAs of homopolymer controls or a series of block copolymers varying in composition, the degree of phase mixing is difficult to quantify.

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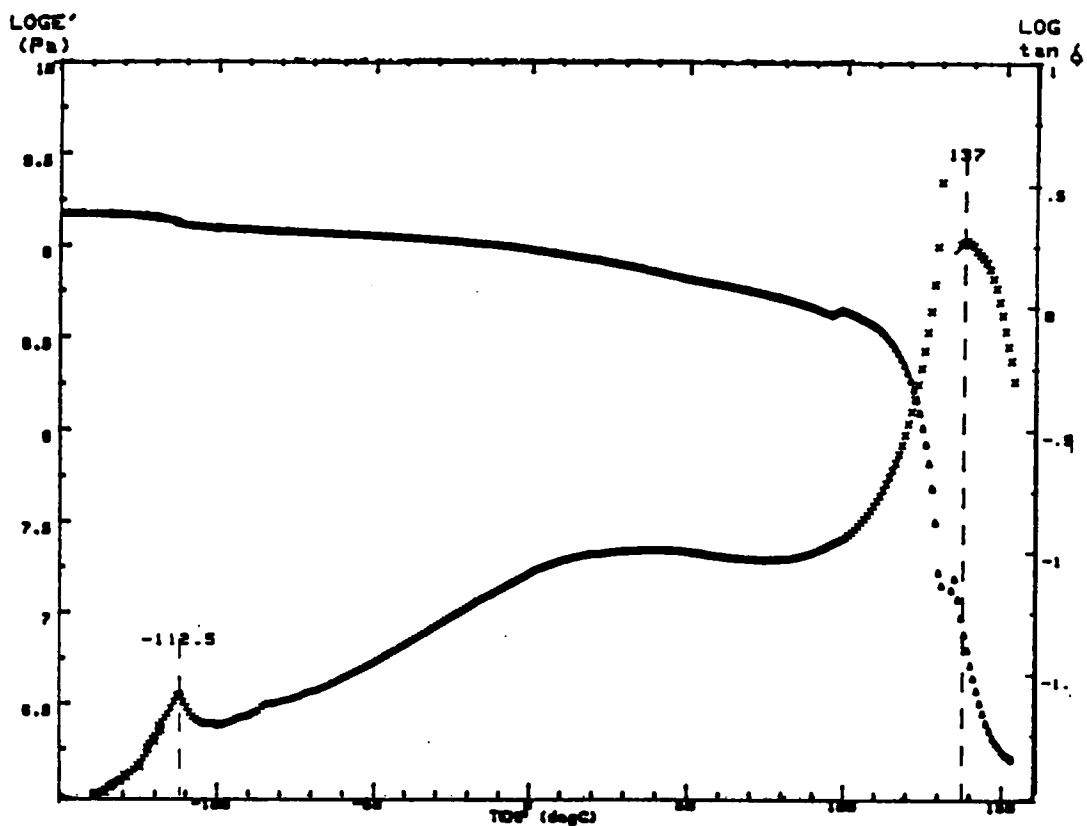


Figure 34. DMTA of a PDMS-b-PMMA Copolymer from a Compression Molded Film.

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COPOLYMERS OF PMMA-G-PDMS.

INTRODUCTION. Though research involving the preparation of block copolymers of PMMA and PDMS has been relatively limited, the preparation of graft copolymers with the aforementioned components has been quite extensive [169-172, 224]. Graft copolymers can be obtained by chemical modification, grafting to or from the backbone of the graft copolymer, or from copolymerization reactions using macromonomers [181].

As addressed in the literature review, the Macromer^R technique, as a synthetic tool, provides a means for the preparation of graft copolymers having side chain grafts of predefined molecular weight and polydispersity. Anionic polymerization is the most commonly used method for the preparation of macromers since, by its nature, functionalized oligomers of defined structure can be prepared. A number of researchers have prepared PDMS macromonomers by the anionic ring opening polymerization of the cyclic siloxane trimer (D_3) [168-172]. These macromonomers have been copolymerized with a variety of monomers by free radical and anionic techniques to yield graft copolymers. Though the potential for homopolymer contamination is present, a unique attribute of PMMA-g-PDMS copolymers prepared as described above, is the ability to

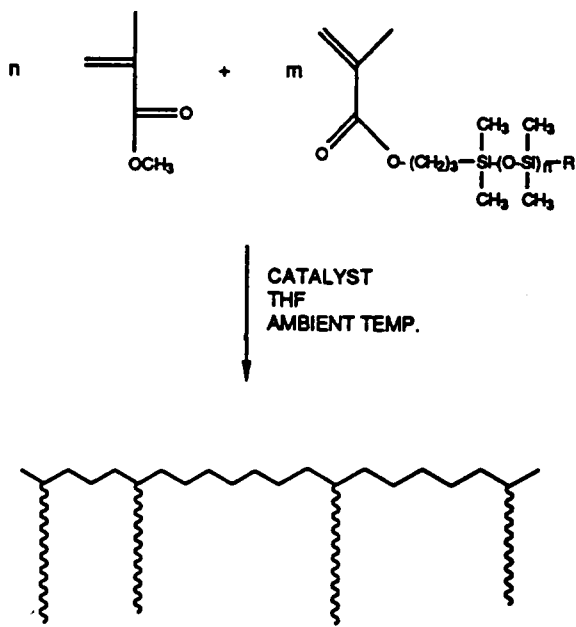
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remove the unincorporated PDMS macromer from the graft copolymer by simple extraction. In the absence of the PDMS homopolymer, use of the Macromer^R method in the preparation of graft copolymers permits the elucidation of additional information regarding the sufficient control of the number of grafts per molecule, and the number average length and polydispersity of each component. These unanswered questions, regarding more precisely the sequence length distribution and chemical composition distribution (CCD), have limited the complete tailoring of graft copolymer materials to specific applications.

PREPARATION OF PMMA-G-PDMS COPOLYMERIZED USING GTP.

Asami previously demonstrated the utility of GTP in the preparation of graft copolymers based on polystyrene and PMMA [81,112]. Though examination of the CCD was not pursued in these studies. Our investigations however, entailed examination of the CCD of PMMA-g-PDMS graft copolymers using GTP as the second copolymerization step (Scheme 25). The PDMS macromers were prepared and characterized as described earlier in this chapter. As in the preparation of PMMA-b-PDMS, in which GTP was utilized as the second copolymerization step, selection of the catalyst was critical to prevent chemical degradation of the PDMS macromonomer during copolymerization. The catalysts used were either tetraethylammonium acetate (TEAA) or

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Scheme 25. Copolymerization of MMA and PDMS Macromer by GTP

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tetrabutylammonium benzoate (TBAB). It must be kept in mind that due to the limited solubility of TEAA in THF it was often difficult to accurately report the actual charge of catalyst, thus, TBAB was the preferred catalyst for preparation of these copolymers.

As depicted in Scheme 25 the copolymerization was carried out at ambient temperature under a nitrogen atmosphere in tetrahydrofuran. The initiator, MTS, followed by the addition of an aliquot of catalyst, was charged to the polymerization vessel already containing a 15-20 wt/v % solution of MMA and PDMS macromer. Unlike the order of addition used in the kinetic investigations and block copolymer studies, initiator and catalyst were not allotted time to form the equilibria activated initiator-catalyst complex, therefore; an induction period was anticipated. The calculated charge of initiator and catalyst were utilized, unlike the aliquot addition of initiator in the anionic copolymerization [170,171] thus, it was anticipated, in the absence of terminating side reactions, that more control over the molecular weight of the copolymer backbone could be maintained.

Like the GTP of block copolymers containing PDMS, the prevalent exotherm typically observed with GTP was again absent. Since a detectable exotherm was usually absent or small, the polymerizations were usually terminated after 2-3 hours by the addition of methanol. The copolymers were

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isolated by precipitation in methanol and dried under vacuum. Prior to characterization of these materials, unincorporated PDMS macromonomer was removed with hexanes using a Soxhlet extractor (Figure 35). Table 31 displays some incorporation data for these copolymers. The apparent $\langle M_n \rangle$ from GPC is also listed, though due to variations in hydrodynamic volume these numbers are of little meaning.

CHEMICAL COMPOSITION DISTRIBUTION (CCD). A significant amount of interest has been generated in the determination of the chemical composition distribution of copolymers. The CCD of copolymers can be expressed as the distribution of the amounts of monomeric units and of the molar masses [10]. It is dependent on two basic factors for small molecules, the compositional feed ratio throughout copolymerization and the statistics of the copolymerization.

Stockmayer [225] developed the original equations to evaluate chemical heterogeneity in copolymers of monomeric units having equivalent molecular weights. But it is not possible with this distribution function equation to determine the chemical heterogeneity arising in systems, such as graft copolymers prepared by the macromonomer technique, in which the components of the copolymerization have unequivalent molecular weights. In order to evaluate the distribution function of the chemical composition of block and graft copolymers, Stejskal and

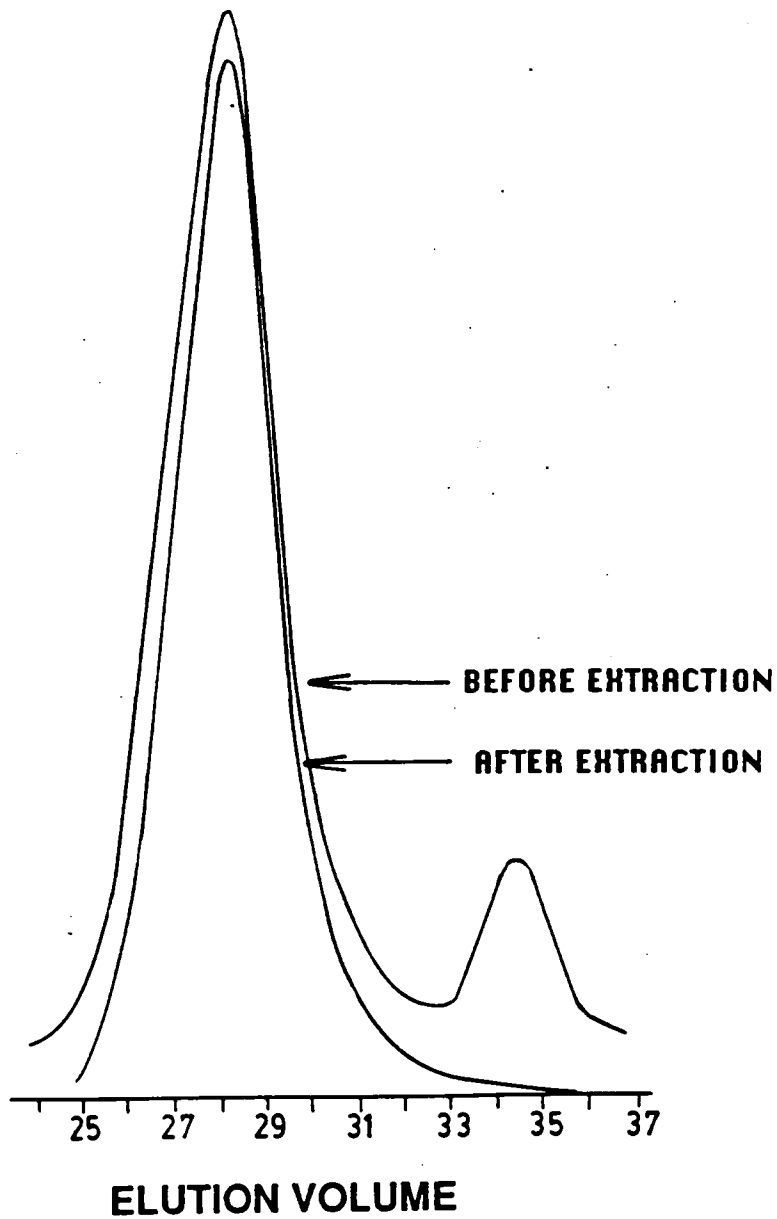


Figure 35. GPC Trace of a PMMA-g-PDMS Copolymer Prepared Using Anionic and GTP Mechanisms

RESULTS AND DISCUSSION

TABLE 31: CHARACTERIZATION OF PMMA-g-PDMS COPOLYMERS

Sample	Macromonomer <Mn> (VPO)	% Recovered Yield ^a	Wt% PDMS ^b	<Mn> ^c	<Mw>/<Mn>
A	3,400	79%	11	92,600	1.45
B	5,500	76%	10	68,200	1.42
C	9,500	73%	10	64,800	1.35

^a After extraction with hexanes

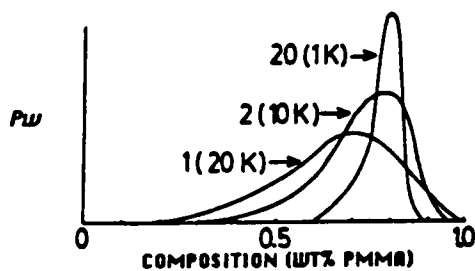
^b ¹H NMR after extraction in CDCl₃ (270 MHz)

^c Apparent <Mn> from GPC using linear PMMA stds.

Kratochvil [227-230] have modified Stockmayer's equation and outlined a theory of CCD to account for monomeric units of different molecular weights. Their theory predicts that the CCD will be a function of both molecular weight and the number of grafts per backbone. Taking advantage of the macromer technique as a model for the polymerization of monomers of unequivalent molecular weight, the theories of Stejskal and Kratochvil predict, at a constant weight percent macromonomer, the breadth of the CCD narrows as the number of grafts is increased, assuming random incorporation of the macromonomer along the backbone (Figure 35) [229]. The weight percent of the graft component is held constant by varying the molecular weight of the macromonomer.

A number of suitable procedures have been reported for the determination of CCD: fractional precipitation [229,230], equilibrium sedimentation [10,231,232], quantitative thin-layer chromatography/flame ionization detection method [234] and super critical fluid extraction (SCFE) fractionation [36,170,171]. The fractions obtained from each of these procedures are not homogeneous with respect to the measured property, but also possess a distribution [10,234]. This was recently demonstrated with the fractionation of polydimethylsiloxane oligomers using SCFE. The GPC trace of each fraction represents a narrow cut of the parent material, and the total combination of traces

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EXAMPLE:

IF MW = 100,000 g/mol, 20 wt% PDMS, 80 wt% PMMA

IF MACROMER MW = 1,000 g/mol

$$\frac{20,000}{1,000} = 20 \text{ GRAFTS/BACKBONE}$$

IF MACROMER MW = 10,000 g/mol

$$\frac{20,000}{10,000} = 2 \text{ GRAFTS/BACKBONE}$$

IF MACROMER MW = 20,000 g/mol

$$\frac{20,000}{20,000} = 1 \text{ GRAFT/BACKBONE}$$

229. Stejskal, J; Kratochvil, P.; Jenkins, A.D.
Macromolecules, 1987, 20(1), 181.

Figure 35. Modified Stockmayer Distribution Function

overlayed, falls within in boundaries of the trace of the parent material [191,235].

EVALUATION OF THE CCD OF PMMA-g-PDMS COPOLYMERS. Based on the theories of Stejskal and Krotchvil for graft copolymers prepared by the macromonomer technique, the CCD predicted by the model should have a Zimm-Schultz distribution of degrees of polymerization. The CCD can be demonstrated by plotting the cumulative weight fraction of copolymer vs composition with each point representing a fraction of the parent copolymer obtained from the fractionation procedure. Using free radical polymerization techniques to incorporate various weight percents of PDMS macromer into a PMMA backbone, experimental evidence was found to support the claim that the breadth of the CCD decreases as the number of grafts per backbone increases [230]. The results, plotted as the cumulative weight fraction verses composition (determined from ^1H NMR), were obtained from fractionation of the copolymers using SCFE methods.

Though most fractionation methods are plagued by laborious and time consuming methodologies, super critical fluid extraction, with the ability to accommodate large sample sizes and the use of various extraction solvents, can be presented as a unique alternative [236]. A number of researchers have collaborated to determine the efficiency of

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SCFE for the determination of CCD information. Comparing fractionation results obtained from SCFE and demixing solvent fraction, DeSimone et al. have determined the CCD for PMMA-g-PDMS copolymers identical in structure and composition. The correlation of fractionation results demonstrated the efficiency of both techniques for the determination of CCD information [170].

The fractionation studies using PMMA-g-PDMS copolymers elucidated an even more valuable piece of information. That is, the effect of the polymerization mechanism in the copolymerization of monomer and macromer. As expected from the nature of homopolymerizations, the use of free radical routes in the second step of the copolymerization affords graft structures of relatively broad compositional and molecular weight distribution [36,170,171,226]. On the other hand, the results indicate, that the CCD for an anionically prepared graft copolymer is substantially more uniform [170,171].

CCD OF PMMA-G-PDMS COPOLYMERS PREPARED BY GTP. From these previous studies, curiosity rose as to the CCD in graft copolymers using GTP for the copolymerization of MMA and PDMS methacryloxy terminated macromers. One would anticipate that the results should mimic those achieved using anionic polymerization. Both mechanism are described as living. Ideally then, a Poisson molecular weight

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distribution for the backbone of the copolymer should yield a narrow CCD upon fractionation of the material.

In a collaborative effort with workers at Phasex Corporation, the graft copolymers prepared via GTP were fractionated using sequential extractions with chlorodifluoromethane above its supercritical temperature and pressure ($T_c = 96^\circ\text{C}$, $P_c = 716\text{ psia}$). Upon fractionation, the samples were then evaluated by NMR, to determine the siloxane content, and size exclusion chromatography. From the NMR data and the weight fraction of each fraction (Table 32), the CCD would have been determined as described previously. However, from the information supplied by GPC, an interesting peculiarity was observed from the fractionation results. It is important to reiterate here that fractionation methods, including SCFE, yield samples which are not homogeneous and thus themselves possess a distribution of molecular weights and compositions [10,234]. Concentrating on the results for the fractionation of PMMA-g-PDMS, the GPC traces of the early fractions were clearly bimodal and in some instances multimodal (Figure 37). This phenomenon was continuously observed only in the fractionation of graft copolymer samples in which GTP was used as the copolymerization mechanism and would not have been anticipated recalling the apparent narrow distribution of the parent materials prepared using GTP.

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TABLE 32: SCFE DATA OF A PMMA-G-PDMS COPOLYMER

Fraction ^a	g(collected)	Wt%	Wt% PDMS ^b
1	0.52	6.3	36.0
2	0.70	8.5	24.0
3	1.30	15.9	7.5
4	2.21	27.0	4.7
5	1.03	12.6	4.0
6	0.58	7.1	4.4
7	0.61	7.4	3.9
8	1.24	15.1	3.5

^a Parent Copolymer: 10wt% PDMS (¹H NMR)
 <Mn> of PDMS macromer = 20,800 g/mol
 <Mw>/<Mn> = 1.07

^b Determined by ¹H NMR (270 MHz) in CDCl₃

RESULTS AND DISCUSSION

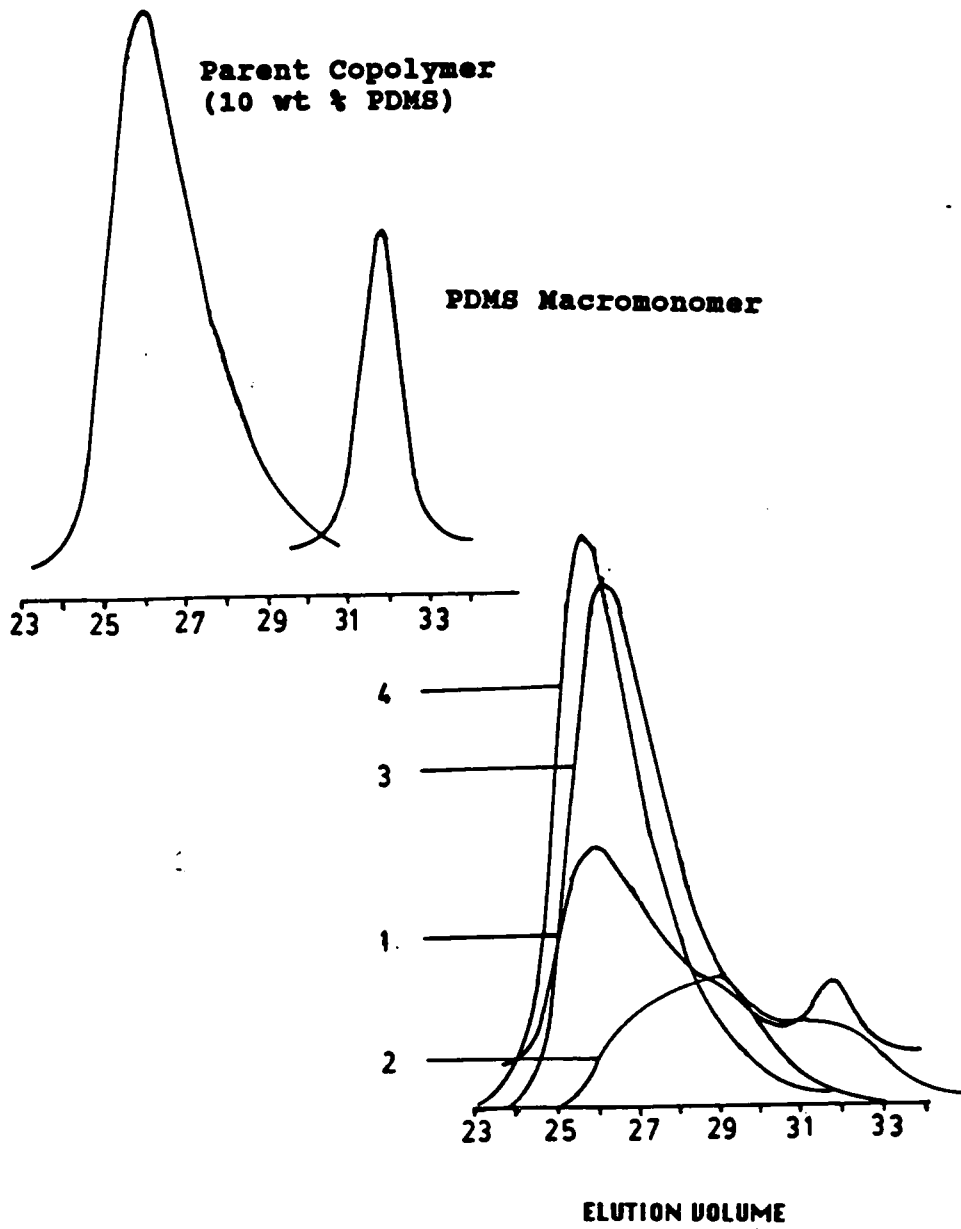


Figure 36. GPC Traces of a Fractionated PMMA-g-PDMS Copolymer

RESULTS AND DISCUSSION

In latter extraction studies, carbon dioxide was used as a extraction solvent to remove any homopolymer PDMS macromer that may have been present after extraction in hexanes. Again the same anomaly was observed. Even with the tedious control of pressure profiling during fractionation, the GPC traces of early fractions indicated this unusual anomaly.

An explanation, which stems from the facts visualized by the GPC traces, is related to the composition of the material. More specifically, materials of different composition and different molecular weights may be soluble under the same SCFE conditions. If this is true, then the evidence seems to be directed to the mechanism of GTP.

The most apparent difference between GTP and anionic mechanisms is the presence of a silicon atom. The mechanism of GTP, as discussed previously, intricately revolves around this atom. It may be possible that the presence of PDMS interferes with the normal rate of propagation, in that the silicon atoms along the backbone act as an alternate site for catalyst coordination. This would alter the level of catalyst available for polymerization and cause a reduction in the rate of polymerization.

Without performing kinetic studies, this possibility of competitive inhibition was examined using a nonfunctional PDMS oligomer. Table 33 displays the results of two GTP of MMA. The polymerizations were permitted to proceed under

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TABLE 33: EFFECT OF PDMS ON THE GTP OF MMA

Sample	MW(TH)	$\langle Mn \rangle^a$	$\langle Mn \rangle / \langle Mw \rangle$	Yield
PMMA	50,000	23,500	1.13	78%
PMMA/PDMS	50,000	16,800	1.19	

^a GPC results based on PMMA stds.

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identical conditions for the same amount of time, during which the exotherms of polymerization were monitored. In the presence of a nonfunctional PDMS oligomer an exotherm was detected and maintained, though it was not as dramatic as the exotherm for the control. It is difficult on the basis of yield to determine the extent of reaction as seen from the results of ^1H NMR of the material. 20 wt% PDMS oligomer was initially charged, and NMR, prior to extraction, indicates 8 wt% PDMS present in the recovered polymer. After extraction; however, ^1H NMR does indicate the efficient removal of PDMS oligomer from the PMMA homopolymer by simple extraction with hexanes.

The GPC results on the other hand do give some indication that the PDMS may interfere with the rate of polymerization. Both homopolymers have relatively narrow molecular weight distributions which is an indication that termination over time is not occurring to any appreciable extent due to impurities introduced with the PDMS oligomer. As indicated from the $\langle M_n \rangle$, the extent of polymerization for the homopolymer prepared in the presence of PDMS is much less than the control even though polymerizations proceeded over the same time frame and virtually under the same reaction conditions. This qualitative experiment indicates that the effective amount of catalyst available is drastically reduced. Further investigations to elucidate if competitive inhibition is playing a role in GTP when

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siloxane oligomers are present; e.g. block and graft copolymers, would involve kinetic studies to determine the effect of varying concentrations of siloxane containing species, such as hexamethyldisiloxane.

Despite the unusual fractionation behavior of these PMMA-g-PDMS copolymers some further characterization involving DMTA, thermal gravimetric analysis (TGA) and XPS was performed on these materials. The low temperature transition (-120 °C) corresponding to the T_g of PDMS component is clearly shown in Figure 37, though determination of the upper T_g was not obtained. Again it is difficult to speculate on the potential degree of phase mixing from a single DMTA without analyzing controls or a series of copolymers varying in composition and graft molecular weight.

TGA analysis provided more preliminary information on polymer structure (Figure 38). Firstly, the thermal stability of PMMA ($\langle M_n \rangle = 101,000$ g/mo) prepared by GTP shows the same behavior as anionically prepared PMMA. This would be expected due to the presence of saturated end groups in contrast to free radically polymerized PMMA having unsaturated end groups and head to head linkages which significantly effect the thermal stability of these materials [35]. The presence of PDMS (17 wt% of 20K oligomer) does appear to enhance the thermal stability of the copolymer but not to the obvious degree noted for the

RESULTS AND DISCUSSION

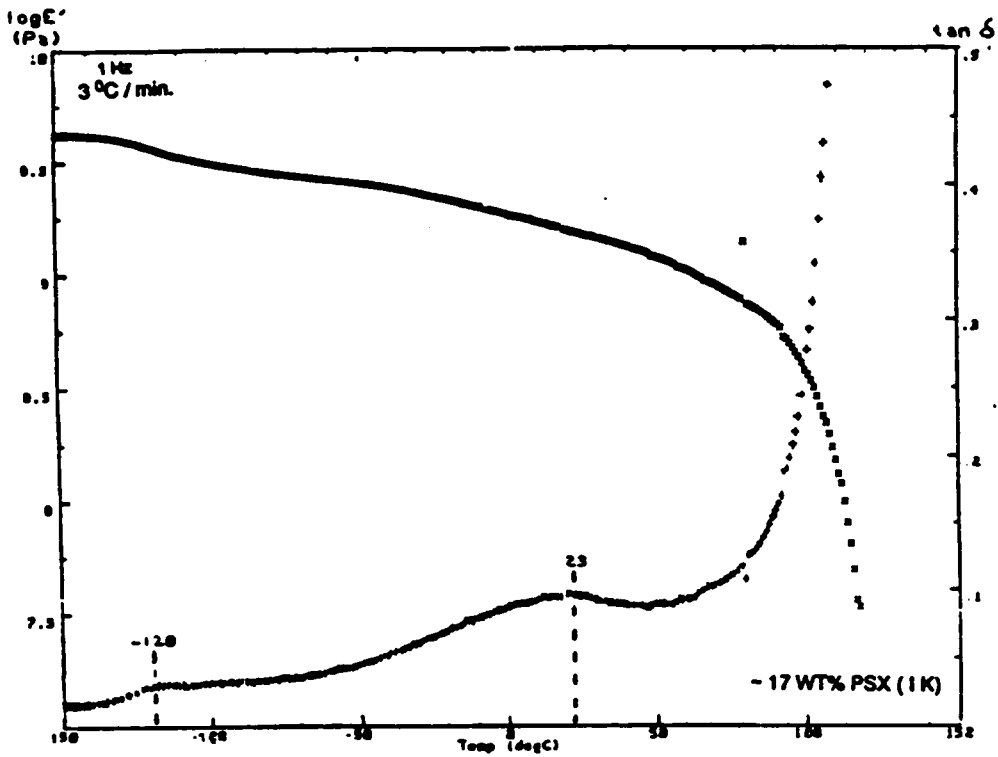


Figure 37. DMTA of PMMA-g-PDMS prepared using GTP

RESULTS AND DISCUSSION

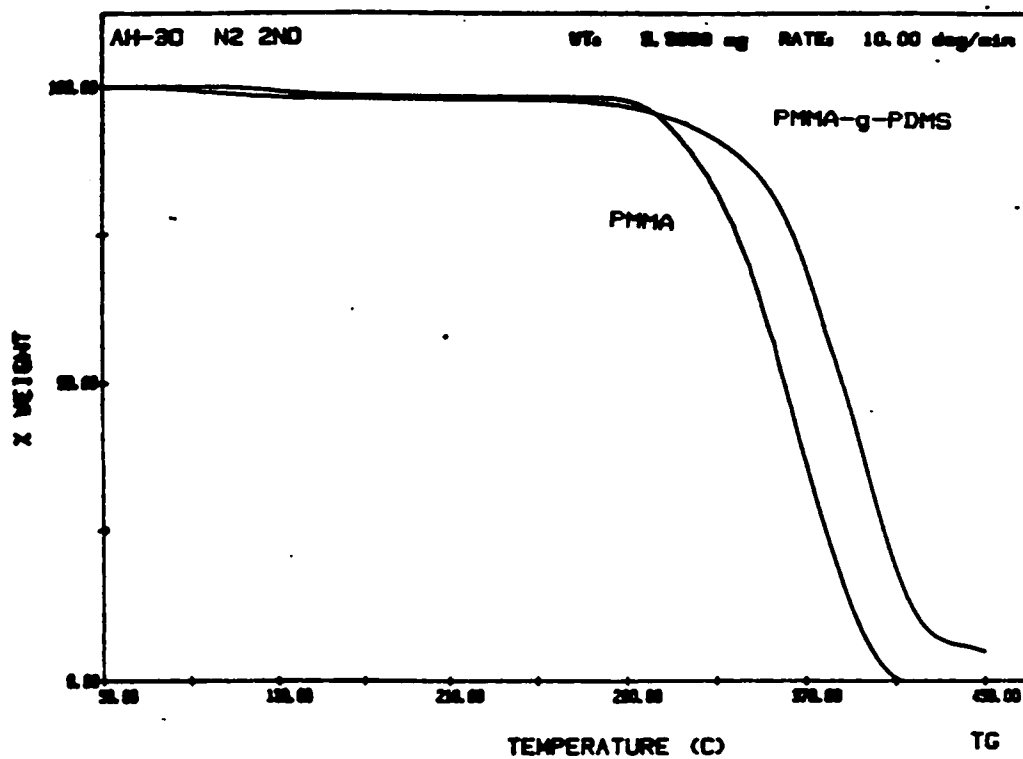


Figure 38. Comparison of the Thermal Stability of PMMA-g-PDMS copolymers relative to PMMA

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free radical copolymers of MMA and methacryloxy functional PDMS [36].

In addition these materials were analyzed using variable Angle XPS. The composition of the surface, in terms of the weight percent PDMS can be quantified as a function of depth into the surface. Table 34 summarizes preliminary results obtained for graft copolymers of ~20 wt% PDMS but varying graft molecular weights. As the depth profiling angle decreases there is an increase in the siloxane content as would be anticipated due to the lower surface free energy.

TABLE 34: DEPENDENCE OF SURFACE COMPOSITION ON SILOXANE MOLECULAR WEIGHT AND COMPOSITION

Macromer Mwt ^a	%PDMS at various angles ^b		
	15°	30°	90°
1,000	60	44	35
5,000	75	57	47
10,000	72	53	45

^a PMMA-g-PDMS (~20 wt%)

^b Variable angle XPS (ESCA), %PDMS based on atomic concentrations

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CHAPTER V**CONCLUSIONS**

From the investigations described throughout this dissertation a number of conclusions can be drawn. Firstly, the command of the GTP methodology was demonstrated from the controlled studies involving alkyl methacrylates, primarily MMA. The sensitivity of the polymerization mechanism to termination by protic impurities confirms the requirement for purification of reagents. The utility of trialkyl aluminums and their derivatives for the purification of alkyl methacrylates enables monomer purity requirements to be obtained for GTP.

More investigations, involving the kinetics of GTP for MMA with TBAB as the selected catalyst, elucidates the complexity of this mechanism. A controlled temperature polymerization reactor was utilized to permit the investigation of both the catalyst and initiator

concentrations on the rate of polymerization while maintaining strict temperature control. Initial studies have shown that the rate of polymerization is significantly influenced by the concentration of catalyst and the mole ratio of initiator relative to catalyst, though it is difficult to make any definitive statements regarding the kinetics or mechanism of GTP. Also, polymerizations performed at various temperatures enabled the calculation of a global energy of activation value for GTP with TBAB as the selected catalyst.

In addition to these studies, research was directed toward the preparation of well-defined copolymers containing PDMS. Functionalized oligomers of PDMS were routinely prepared by the anionic ring opening polymerization of hexamethylcyclotrisiloxane. Though a diverse number of analytical techniques were employed to characterize these oligomers, ^{29}Si NMR was uniquely useful for direct determination of the oligomer functionality, which is equally important to the efficiency of the transformation reaction and the Macromer^R technique. This technique is also useful, as is ^1H NMR, for the characterization of PDMS macroinitiators capable of initiating the GTP of MMA. Copolymers of PDMS and PMMA were prepared through a transformation synthesis involving anionic and GTP mechanisms. Likewise, these mechanisms were again coupled to prepare graft copolymers through the

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copolymerization of MMA with methacrylate terminated PDMS macromonomer. Though the efficiency of the transformation reaction was not quantitative nor the fractionation of the GTP prepared PMMA-g-PDMS copolymers ideal, these studies indicate the presence of a mechanistic limitation. It appears that the PDMS may compete with the initiator or chain end for the catalyst which effectively lowers the active concentration of catalyst and consequently the rate of polymerization.

CONCLUSIONS

CHAPTER VI**SUGGESTED FUTURE STUDIES**

Many future directions exist for the various aspects of this research involving the GTP mechanism. A number of these have been commented upon during the discussion of the results. The major areas which deserve attention will be highlighted below.

- 1) Studies directed to identify the effect of the size of the ester alkyl group and the electronic nature of the methacrylate on the rate of transfer of the silyl group and ease of GTP polymerization of alkyl methacrylates. With these various alkyl methacrylates, one could employ ^{29}Si NMR to potentially identify the formation of the hexacoordinate silicon intermediate proposed in the concerted associative mechanism.

2) The preparation of various ketene silyl acetal initiators (e.g. steric variations etc.) and terminating reagents to enable the preparation of well-defined chelic and telechelic copolymers for further use in post reactions, e.g. initiators based on t-butyl methacrylate and maleimides.

3) The preparation of all-methacrylic thermoplastic elastomers via GTP and the study of the physical properties of a series of copolymers varying in composition. In addition the preparation characterization of alkyl methacrylate based ionomers by GTP and the corresponding telechelic ionomers using a functional ketene silyl acetal.

4) Continued studies of the kinetics of GTP. In particular, examination of the effect of the mole ratio of initiator to catalyst. It may be possible to define, for a selected catalyst, the range or region in which the rate of monomer addition no longer is strictly the rate determining step.

5) Kinetics of the GTP of various alkyl acrylate monomers to elucidate the role of Lewis acid catalysts, and define a connecting GTP mechanism for nucleophilic and electrophilic catalysts.

SUGGESTED FUTURE STUDIES

6) Kinetic investigations involving determination of the effect of the concentration of a competitive inhibitor, such as hexamethyldisiloxane, on the rate of polymerization.

7) Upon understanding the nature of the competitive inhibition, prepare PMMA-b-PDMS copolymers of varying composition and examine in more detail the morphology and physical properties of these materials. Preparation of difunctional macroinitiators easily leads to the preparation of thermoplastic elastomers based on PMMA and PDMS.

CHAPTER VII

LITERATURE CITED

1. Hochheiser, S. Today's Chemist 1988, 1 (3), 8-10.
2. Kine, B.B.; Novak, R.W. In Encyclopedia of Chemical Technology; 3rd ed.; Vol. 1; John Wiley & Sons: New York, 1985, 235-299.
3. Mark, H. Polym. Plast. Technol. Eng. 1986, 25(1), 1.
4. Seymour, R.B.; Carraher, C.E. Structure-Property Relationships in Polymers; Plenum: New York, 1984.
5. Long, T.E.; Allen, R.D.; McGrath, J.E. In Recent Advances in Mechanistic and Synthetic Aspects of Polymerization; Fontanille, M., and Guyto, A., Eds.; NATO ACS Series 215; D. Reidel Publishing Co.: Dordrecht, Holland, 1987; pp 79-100.
6. Herold, F.K.; Schulz, G.V.; Wolf, B.A. Polymer Communications 1986, 27, 59.
7. Li, B.Y.; Jiang, D.Z.; Fytas, G.; Wang, C.H. Macromolecules 1986, 19(3), 778.
8. Tribone, J.J.; O'Reilly, J.M.; Greener, J. Macromolecules 1986, 19(6), 1732.
9. Bovey, F.A. Macromol. Chem., Macromol. Symp. 1988, 20/21, 105.
10. Elias, H.G. Macromolecules: Structure and Properties; 2nd ed.; Plenum: New York, 1984.

11. Yuki, H.; Hatada, K. In Advances in Polymer Science; Cantow, H.J., Ed.; Springer-Verlag: New York, 1979; Vol.31, pp. 1-45.
12. Allen, P.E.M.; Host, D.M.; Truong, V.T.; Williams, D.R.G. Eur. Polym. J. 1985, 21(7), 603.
13. Bovey, F.A. Chain Structure and Conformation of Macromolecules; Academic Press: New York, 1982.
14. Fox, T.G.; Garrett, B.S.; Goode, W.E.; Gratch, S.; Kincaid, J.F.; Spell, A.; Stroupe, J.D. J. Am. Chem. Soc. 1958, 80, 1768.
15. Erusalimskii, B.L. Mechanisms of Ionic Polymerization: Current Problems; Consultants Bureau: New York, 1986.
16. Hatada, K.; Sugino, H.; Ise, H.; Kitayama, T.; Okamoto, Y.; Yuki, H. Polym. J. 1980, 12(1), 55.
17. Truong, V.T.; Allen, P.E.M.; Williams, D.G. Eur. Polym. J. 1987, 23(3), 181.
18. Doherty, M.A.; Hogen-Esch, T. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1984, 25(2), 5-6.
19. Katime, I.A.; Quintana, J.R. Polym. J. 1988, 20(6), 458-469.
20. Katime, I.A.; Quintana, J.R. Eur. Polym. J. 1988, 24(8), 775-782.
21. Allen, G. Polym. J. 1987, 19(1), 1.
22. March, J. Advanced Organic Chemistry: Reactions, Mechanisms and Structure; 2nd ed., McGraw Hill Book: New York, 1977.
23. McGrath, J.E. J. Chem Ed. 1981, 844.
24. Elias, H.G. Macromolecules: Synthesis, Materials and Technology; 2nd ed.; Plenum: New York, 1984.
25. Odian, G. Principles of Polymerization, 2nd ed.; John-Wiley and Sons: New York, 1981.
26. Bevington, J.C. Makromol. Chem., Macromol. Symp. 1988, 20, 59.

LITERATURE CITED.

27. Allen, N.S.; Catalina, F.; Green, P.N.; Green, W.A. Eur. Polym. J. 1986, 22(1), 49.
28. Sato, T.; Abe, M.; Otsu, T. Makromol. Chem. 1977, 178, 1951.
29. Hatada, K.; Kitayama, T.; Masuda, E. Polym. J. 1986, 18(5), 395.
30. Yuki, H.; Hatada, K.; Kikuchi, Y.; Niinomi, T. Polym. Lett. 1968, 6, 753.
31. Challa C.; Tan, Y.Y. J. App. Chem. 1981, 53, 627.
32. Srivastava, A.K.; Nigam, S.K.; Shukla, A.K.; Saini, S.; Kumar, P.; Tewari, N. Rev. Macromol. Chem Phys. 1987, C27(2), 171.
33. Malavasic, T.; Osredkar, U.; Anzur, I.; Vizovisek, I. J. Macromol. Sci.-Chem. 1985 A25(1), 55.
34. Fehervari, A.; Boros Geyevi, E.; Foldes-Berezsich, T. J. Macromol Sci. -Chem. 1982, A18(3), 431
35. Kashiwagi, T.; Inaba, A.; Brown, J.; Hatada, K.; Kitayama, T.; Masuda, E. Macromolecules 1986, 19, 2160.
36. Smith, S.D. Ph.D. Dissertation, Virginia Polytechnic and State University, 1987.
37. Hsieh, H.L.; Farrar, R.C.; Udipi, K. In Anionic Polymerization: Kinetics, Mechanism, and Synthesis; McGrath, J.E., Ed.; ACS Symposium Series 166; American Chemical Society: Washington, DC, 1981; 389-407.
38. Halasa, A.F. In Anionic Polymerization: Kinetics, Mechanisms, and Synthesis; McGrath, J.E., Ed.; ACS Symposium Series 166; American Chemical Society: Washington, DC, 1981; 409-426.
39. Long, T.E. .D. Dissertation, Virginia Polytechnic and State University, 1987.
40. Müller, A.H.E. In Anionic Polymerization: Kinetics, Mechanism, and Synthesis; McGrath, J.E.,

- Ed.; ACS Symposium Series 166; American Chemical Society: Washington DC, 1981; 441-461.
41. Bywater, S., In Encyclopedia of Chemical Technology; 3rd ed.; Vol. 2; John Wiley & Sons: New York, 1985. 1-43.
 42. Tomoi, M.; Sekiya, K.; Kakiuch, H. Polym. J. 1974, 6(5), 438-444.
 43. Hatada, K.; Kitayama, T.; Fumikawa, K.; Ohta, K.; Yuki, H. In Anionic Polymerization: Kinetics, Mechanisms, and Synthesis; McGrath, J.E., Ed.; ACS Symposium Series 166; American Chemical Society: Washington DC, 1981; 327-341.
 44. Kitayama, T.; Ute, K.; Hatada, K. Polym. J. 1984, 16(12), 925-928.
 45. Freyes, D.; Rempp, P.; Benoit, H. J. Polym. Sci. Letters, 1964, 2, 217.
 46. Wiles, D.M.; Bywater, S. Trans. Fara. Soc. 1965, 61, 150.
 47. Long, T.E.; Allen, R.D.; McGrath, J.E. In Recent Advances in Mechanistic and Synthetic Aspects of Polymerization; Fontanille, M., and Guyto, A., Eds.; NATO ACS Series 215; D. Reidel Publishing Co.: Dordrecht, Holland, 1987; pp 79-100.
 48. Allen, R.D.; Long, T.E.; McGrath, J.E. Polym. Bull. 1986, 15, 127-134.
 49. Allen, R.D. Ph.D. Dissertation, Virginia Polytechnic and State University, 1985.
 50. Allen, R.D.; Long, T.E.; McGrath, J.E. In Advances in Polymer Synthesis; Culbertson, B.M.; Ed.; Vol 31.; Plenum: 1985, p 347.
 51. Allen, P.E.M.; Mair, C.; Fisher, M.C.; Williams, E.H. J. Macromol. Sci. -Chem. 1982, A17(1), 61-76.
 52. Raynal, S. J. Macromol. Sci. -Chem. 1982, A18(3), 313-322.
 53. Berger, W.; Adler, H.J. Makromol. Chem., Macromol. Symp. 1986, 3, 301-316.

54. Müller, A.H.E.; Höcker, H.; Schulz, G.V. Macromolecules 1977, 10(5), 1086-1089.
55. Müller, A.H.E. Macromol. Chem. 1986, 187, 1473-1482.
56. Warzelhan, V.; Höcker, H.; Schulz, G.V. Makromol. Chem. 1978, 179, 2221-2240.
57. Busfield, W.K.; Methven, J.M. Polymer 1973, 14, 137.
58. Kitano, T.; Fujimoto, T.; Nagasawa, M. Polym. J. 1977, 9(2), 153-159.
59. Chiellini, E.; Nocci, R. J. Polym. Sci., Polym Chem. Ed. 1973, 11, 493-505.
60. Jerome, R.; Forte, R.; Varshney, S.K.; Fayt, R.; P Teyssie In Recent Advances in Mechanistic Aspects of Polymerization; Fontanille, M. and Guyot, A., Eds.; NATO ACS Series 215; D. Reidel Publishing Co.: Dordrecht, Holland, 1987, pp 101-117.
61. Fayt, R.; Forte, R.; Jacobs, C.; Jerome, R.; Ouhadi, T.; Teyssie, Ph.; Varshney, S.K. Macromolecules 1987, 20(6), 1442-1444.
62. Teyssie, Ph.; Fayt, R.; Jacobs, C.; Jerome, R.; Leemans, L. and Varsney, S. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1988, 29(2), 52-53.
63. DeSimone, J.M.; Hellstern, A.M.; McGrath, J.E. unpublished results.
64. Boettcher, F.P. J. Macromol. Sci. Chem. 1985, A22(5-7), 665-678.
65. Riess, G.; Hurtrez, G.; Bahadur, P. Encyclo. Poly. Sci. and Tech., 3rd ed., 1985, 2, 324-434.
66. Webster, O.W.; Hertler, W.R.; Sogah, D.Y.; Farnham, W.B.; RajanBabu, T.V. J. Am. Chem. Soc. 1983, 105(17), 5706-5709.
67. Webster, O.W. U.S. Patent 4 508 880, (to duPont) 1985.
68. Webster, O.W.; Sogah, D.Y. In Recent Advances In Mechanistic and Synthetic Aspects of Polymerization; Fontanille, M., and Guyot, A., Eds.;

NATO ASI Series 215; D. Reidel Publishing:
Dordrecht, Holland. 1987; pp. 3-21.

69. Ainsworth, C.; Chen, F.; Kuo, Y. J. Organomet. Chem **1972**, 46, 59-71.
70. Kita, Y.; Haruta, J.; Segawa, J.; Tamura, Y. Tetrahedron Lett. **1979**, 44, 4311-4314.
71. Yoshii, E.; Takeda, K. Chem. Pharm. Bull. **1983**, 31(12) 4586-4588.
72. Ojima, .; Kumagai, M.; Nagai, Y. J Organomet. Chem. **1976**, 111, 43-60.
73. Corey, J.Y In Organometallic Chemistry Reviews; Annual Surveys: Si, Sb, Bi, Mn, Tc, Re, Heteronuclear Complexes; King, R.B. and Oliver, J.P., Eds.; J. Organometal Chem Library 17; Elsevier Science: New York, 1985; 163-309.
74. Ikeda, K.; Achiwa, K.; Sekiya, M. Tetrahedron Lett. **1983**, 24(43), 4707-4710.
75. Kita, Y.; Segawa, J.; Haruta, J.; Fujii, T.; Tamura, Y. Tetrahedron Lett. **1980**, 21, 3779-3782.
76. Lutsenko, I.; Baukov, Y.; Burlachenko, G.; Khasapov, B. J. Organomet. Chem. **1966**, 5, 20-28.
77. Sogah, D.Y.; Hertler, W.R.; Webster, O.W.; Cohen, G.M. Macromolecules **1987**, 20, 1473-1488.
78. Sogah, D.Y.; Webster, O.W. J. Polym. Sci. Polym Lett. Ed. **1983**, 21, 927-931.
79. Webster, O.W In Encyclopedia of Chemical Technology; 3rd ed.; Vol. 7; John Wiley & Sons: New York, 1987. 580-588.
80. Cohen, G.M. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Sci.) **1988**, 29(20), 46-47.
81. Asami, R.; Kondo, Y.; Takaki, M. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) **1986**, 27(1), 186-187.
82. Hertler, W.R. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) **1986**, 27(1), 165-166.

83. Yu, H.S.; Choi, W.J.; Lim, K.T.; Choi, S.K. Macromolecules 1988, 21, 2893-2894.
84. Sogah, D.Y. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 1988 29(2), 3-5.
85. Bandermann, F.; Speikamp, H.D. Makromol. Chem., Rapid Commun. 1985, 6, 335-339.
86. Reetz, M.T.; Ostarek, R.; Piejko, K.E.; Arlt, D.; Bömer, B. Angew. Chem. 1986, 25, 1108-1109.
87. Speikamp, H.D.; Bandermann, F. Macromol. Chem. 1988, 189, 437-445.
88. Bandermann, F.; Witkowski, R. Macromol. Chem. 1986,
89. Webster, O.W.; Sogah, D.Y. E.P.O. Application 145 263, 1985.
90. Farnham, W.B. U.S. Patent 4 581 428, (to duPont) 1986.
91. Sitz, H.D.; Bandermann, F. In Recent Advances In Mechanistic and Synthetic Aspects of Polymerization; Fontanille, M., and Guyot, A., Eds.; NATO ASI Series 215; D. Reidel Publishing: Dordrecht, Holland. 1987; pp. 41-47.
92. Dicker, I.B.; Cohen, G.M.; Farnham, W.B.; Hertler, W.R.; Lagasnis, E.D.; Sogah, D.Y. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1987, 28(1), 106-107.
93. Hertler, W.R.; Sogah, D.Y.; Webster, O.W. Macromolecules 1984, 17, 1417-1419.
94. Greene, T. Protective Groups In Organic Synthesis; John Wiley & Sons: New York, 1982.
95. Corriu, R.J.P.; Perz, R.; Reye, C. Tetrahedron 1983 39, 999-1009.
96. Kita, Y.; Yasuda, H.; Haruta, J.; Segawa, J.; Tamura, Y. Synth. Commun. 1982, 1089-1091.
97. Middleton, W.J. Organic Synthesis 1986, 60, 221-225.
98. Miller, J.; Jenkins, A.D.; Tsartolia, E.; Walton, D.R.M.; Stejskal, J.; Kratochvil, P. Polym. Bull. 1988, 20, 247-248.

99. Webster, O.W. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1986, 27(1), 161-162.
100. Mukaiyama, T. Angew. Chem. Int. 1977, 16, 817-826.
101. Jacobsen, E.N.; Totten, G.E.; Karydas, A.C.; Rhodes, Y.E. Synth. Commun. 1983, 13(6), 449-458.
102. Miyashita, M.; Kumazawa, T.; Yoshikoshi, A.; Chem. Lett. 1980, 1043-1044.
103. Hutchins, C.S. U.S. Patent 4 656 226, (to duPont) 1987.
104. Gomez, P.M.; Neidlinger, H.N. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1987, 28(1), 209-210.
105. Stinson, S. Chem. Eng. News 1987, 4(16), 43-46.
106. Kozakiewski, J.J.; Kurose, N.S.; Draney, D.R.; Huang, S.Y.; Falzone, J. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1987, 28(2), 347-348.
107. Pugh, C.; Percec, V. Polym. Bull. 1985, 14(2), 109-116.
108. Jenkins, A.D.; Tsartolia, E.; Walton, D.R.M.; Stejska, J.; Kratochvil, P. Polym. Bull. 1988, 20, 97-100.
109. Pugh, C.R.; Percec, V. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1985, 26(2), 303-305.
110. Krueder, W.; Webster, O. Makromol. Chem., Rapid Commun. 1986, 7, 5-13.
111. Suenaga, J.; Sutherlin, D.M.; Stille, J.K. Macromolecules 1984, 17, 2913-2916.
112. Asami, R.; Takaki, M.; Moriyama, Y. Polym. Bull. 1986, 16, 125-130.
113. Sogah, D.Y.; Webster, O.W. In Recent Advances In Mechanistic and Synthetic Aspects of Polymerization; Fontanille, M., and Guyot, A., Eds.; NATO ASI Series 215; D. Reidel Publishing: Dordrecht, Holland. 1987; pp 61-72.
114. Boettcher, F.P. Makromol. Chem., Macromol. Symp. 1988, 13/14, 193-202.

115. Sogah, D.Y.; Farnham, W.B. In Organosilicon and Bioorganosilicon Chemistry; Sakurai, H. Ed.; John Wiley & Sons: New York, 1985; Chapter 20.
116. Farnham, W.B.; Sogah, D.Y. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 1986, 27(1), 167-168.
117. Cella, J.; Cargioli, J.; Williams, E. J. Organometal. Chem. 1980, 186, 13-17.
118. Farnham, W.B.; Whitney, J.F. J. Am. Chem. Soc. 1984, 106, 3992-3994.
119. Corriu, R.J.P. In Recent Advances In Mechanistic and Synthetic Aspects of Polymerization; Fontanille, M., and Guyot, A., Eds.; NATO ASI Series 215; D. Reidel Publishing: Dordrecht, Holland. 1987; pp. 49-60.
120. Sitz, H.D.; Speikamp, H.D.; Bandermann, F. Makromol. Chem. 1988, 189, 429-435.
121. Bandermann, F.; Sitz, H.D.; Speikamp, H.D. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1986, 27(1), 169-170.
122. Mai, P.M.; Müller, A.H.E. Makromol. Chem., Rapid Commun. 1987, 8, 247-253.
123. Mai, P.M.; Müller, A.H.E. Makromol. Chem., Rapid Commun. 1987, 8, 99-107.
124. Müller, A.H.E. In Recent Advances In Mechanistic and Synthetic Aspects of Polymerization; Fontanille, M., and Guyot, A., Eds.; NATO ASI Series 215; D. Reidel Publishing: Dordrecht, Holland. 1987; pp. 23-40.
125. Doherty, M.A.; Gores, F.; Mai, P.M.; Müller, A.H.E. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1988, 29(2), 73-74.
126. Müller, M.; Stickler, M. Makromol. Chem., Rapid Commun. 1986, 7, 575-583.
127. Banerjee, K.G.; Hohen-Esch, T. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1987, 28(2), 320-321.
128. Brittain, W.J. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1988, 29(2), 312-313.

129. Hertler, W.R. *Macromolecules* **1987**, 20(12), 2978-2982.
130. Hertler, W.R. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Sci.)* **1987**, 28(1), 108-109.
131. Sogah, D.Y.; Webster, O.W. *Macromolecules* **1986**, 19(6), 1775-1777.
132. Sogah, D.Y. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Sci.)* **1986**, 27(1), 163-164.
133. Noshay, A.; McGrath, J.E. *Block Copolymers: Overview and Critical Survey*; Academic: New York, 1977.
134. Cowie, J.M.G. *Polymers: Chemistry and Physics of Modern Materials*; Intertext: 1973, pp. 263-291.
135. Bühler, W.; Gronski, W. *Makromol. Chem.* **1988**, 189, 1087-1095.
136. Kine, B.B.; Novak, R.W. In *Encyclopedia of Chemical Technology*; 3rd ed.; Vol. 8; John Wiley & Sons: New York, 1987.
137. McGrath, J.E. *J. Chem. Ed.* **1981**, 58, 914.
138. Wilkes, G.L.; Mody, P.C.; Tant, M.R. *Polym. Eng. Sci.* **1979**, 19(14) 1029-1041.
139. Rempp, P.; Franta, e.; Herz, J. In *Anionic Polymerization: Kinetics, Mechanisms, and Synthesis*; McGrath, J.E., Ed.; ACS Symposium Series Vol.166; American Chemical Society: Washington D.C., 1981, pp 59-70.
140. Higashimura, T.; Sawamoto, M. *Makromol. Chem., Suppl.* **1985**, 12, 153-161.
141. Miyamoto, M; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, 17, 2228-2230.
142. Sigwalt, P. *Polym. J.* **1985**, 17(1), 57-71.
143. Otsu, T.; Kuriyama, A. *Polym. J.* **1985**, 17(1), 97-104.
144. Otsu, T.; Kuriyama, A. *J. Macromol. Sci. -Chem.* **1984**, A21(8/9), 961-977.

145. Inoue, S.; Aida, T. Makromol. Chem., Macromol. Symp. 1986, 6, 217-224.
146. Schulz, D.N.; Sanda, J.C.; Willoughby, B.G. In Anionic Polymerization: Kinetics, Mechanisms, and Synthesis; McGrath, J.E., Ed.; ACS Symposium Series Vol.166; American Chemical Society: Washington D.C., 1981, pp. 427-440.
147. Plastics Technology, 1988, 1, 24.
148. Lundberg, R.D. In Encyclopedia of Chemical Technology; 3rd ed.; Vol. 8; John Wiley & Sons: New York, 1978.
149. Weber, L. Makromol. Chem., Macromol. Symp. 1986, 3, 317-329.
150. Richards, D.H. In Ring Opening Polymerization: Kinetics, Mechanisms, and Synthesis; McGrath, J.E., Ed.; ACS Symposium Series Vol.286; American Chemical Society: Washington D.C., 1985, pp.87-95.
151. Richards, D.H. Brit. Polym. J. 1980, 12 89.
152. Abadie, M.J.; Ourahmoune, D. Brit. Polym. J. 1987, 19, 247-254.
153. Eastmond, G.C.; Grigor, J. Makromol. Chem., Rapid Commun. 1986, 7, 375-379.
154. Eastmond, G.C.; Parr, K.J.; Woo, J. Polymer 1988, 29, 950-957.
155. Yagci, Y. Polym. Commun. 1986, 27(1), 21-22.
156. Zhang, H.; Feng, X. Makromol. Chem. 1988, 189, 293-298.
157. Niwa, M.; Sako, Y.; Shimizu, M. J. Macromol. Sci. -Chem. 1987, A24(11), 1315-1332.
158. Simionescu, C.I.; Comanita, E.; Harabagiu, V.; Simionescu, B.C. Eur. Polym. J. 1987, 23(11) 921-922.
159. Kazama, H.; Tezuka, Y.; Kiyokazu, I.; Goethals, E.J. Makromol. Chem. 1988, 189, 985-992.

160. Paulus, G.; Jerome, R.; Teyssie, P. Brit. Polym. J. 1987, 19, 361-368.
161. Xie, H.; Chen, X. Polym. J. 1988, 20(2), 153-158.
162. Pietrasanta, Y.; Fleury, E.; Boutevin, B.; Sarraf, L. Polym. Bull. 1986, 15, 107-112.
163. Shit, S.C.; Maiti, S. J. Polym. Sci: Polym. Lett. Ed. 1986, 24, 383-387.
164. Milkovich, R. In Anionic Polymerization: Kinetics, Mechanisms, and Synthesis; McGrath, J.E., Ed.; ACS Symposium Series Vol.166; American Chemical Society: Washington D.C., 1981, pp. 41-57.
165. Rempp, P.; Lutz, P.; Masson, P.; Franta, E. Makromol. Chem., Suppl. 1984, 8, 3-15.
166. Kawakami, Y. In Encyclopedia of Chemical Technology; 3rd ed.; Vol. 9; John Wiley & Sons: New York, 1987, pp. 195-203.
167. Kawakami, Y.; Miki, Y.; Tsuda, T.; Murthy, R.A.N.; Yamashita, Y. Polym. J. 1982, 14(11), 913-917.
168. Cameron, G.; Chislom, M.S. Polymer, 1985, 26, 437.
169. Smith, S.D.; York, G.A.; Dwight, D.W.; McGrath, J.E. Polymer Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1987, 28(1), 458-460.
170. DeSimone, J.M.; et.al. Polymer Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1988, 29(2), 116-119.
171. DeSimone, J.M.; et.al. Polymer Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1988, 29(1), 361-362.
172. Kawakami, Y.; Murthy, R.A.N., Yamashita, Y. Makromol. Chem. 1984, 185, 9-18.
173. Tsukahara, Y.; Tanaka, M.; Yamashita, Y. Polym. J. 1987, 19(9), 1121-1125.
174. Niwa, M Higashi, N. Macromolecules 1988, 21, 1193-1194.
175. Heitz, T; Höcker, H. Makromol. Chem. 1988, 189, 777.
176. Rao, P.R.; Lutz, P.; Lamps, J.P.; Masson, P.; Remp., P.

LITERATURE CITED

- Polymer Bull. 1986, 15, 69-75.
177. Nagasaki, Y.; Tsuruta, Macromolecules 1986, 187, 1583-1591.
 178. Chujo, Y.; Kobaayashi, H.; Yamashita, Y. Polymer J. 1988, 20(5), 407-411.
 179. Schulz, R.C.; Schwarzenbach, E. Makromol. Chem., Macromol. Symp. 1988, 13/14, 495-505.
 180. Aoshima, S.; Ebara, K.; Higashimura, T. Polymer Bull. 1985, 14, 425-431.
 181. Dreyfuss, P.; Quirk, R.P. In Encyclopedia of Chemical Technology; 3rd ed.; Vol. 7; John Wiley & Sons: New York, 1987, pp.551-579.
 182. Morrison, R.T; Boyd, R.N. Organic Chemistry; 3rd ed.; Allen and Bacon: Boston, 1973, p.287.
 183. Burfield, D.R.; Lee, K.H.; Smithers, R.H. J. Org. Chem., 1977, 42(18), 3060-3065.
 184. Fieser, M. Fieser & Fieser's Reagents for Organic Synthesis; John Wiley & Sons: NY, 1982, vol. 11, 1142.
 185. Winkle, M.R.; Lanisinger, J.M.; Ronald, R.C. J. C. S. Chem. Comm. 1980, 87-89.
 186. Gilman, H; Cartledge, F.K.; J. Organometal. Chem 1964, 2, 447.
 187. Hoover, J. Ph.D. Dissertation, Virginia Polytechnic and State University, 1987.
 188. Ernst, C.R.; Spialter, L.; Buell, G.R.; Wilhite, D.L. J. Am. Chem. Soc. 1974, 96(17),
 189. Derome, A.E. Modern NMR Techniques For Chemistry Research; Pergamon: New York, 1987.
 190. Elsbernd, C.S.; Hellstern, A.M.; Siochi, E.J.; DeSimone, J.M. unpublished results.
 191. Elsbernd, C.S. Ph.D. Dissertation, Virginia Polytechnic and State University, 1987.
 192. Greenwood, N.N.; Earnshaw, A. Chemistry of the Elements; Pergamon: New York, 1984.

193. DeSimone, J.M.; Hellstern, A.M. unpublished results.
194. DeSimone, J.M.; Hellstern, A.M.; Siochi, E.J.; Ward, T.C.; McGrath, J.E. Polymer Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1989, 30(1), 000.
195. Siochi, E.J.; DeSimone, J.M.; Hellstern, A.M.; McGrath, J.E.; Ward, T.C. Polymer Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1989, 30(1), 000.
196. Brittan, W.J. J. Am. Chem. Soc. 1988, 110, 7440-7444.
197. Moore, J.W.; Pearson, R.G. Kinetics and Mechanism; John Wiley & Sons: New York, 1981; Chapter 1.
198. Espenson, J.H. Chemical Kinetics and Reaction Mechanisms; McGraw-Hill: New York, 1981, p. 5.
199. Bunnett, J.F. In Investigation of Rates and Mechanisms of Reactions; Bernasconi, C.F. Ed.; John Wiley & Sons: New York, 1986, Part 1, Chapter 3.
200. Keefe, J.R.; Kresge, A.J. In Investigation of Rates and Mechanisms of Reactions; Bernasconi, C.F. Ed.; John Wiley & Sons: New York, 1986, Part 1, Chapter 11.
201. Ward, T.C. J. Chem. Ed., 1981, 867-879.
202. Saam, J.C.; Ward, A.H.; Gordon Fearon, F.W.; Polym. Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1972, 13(1), 524-528.
203. Hsu, T.; Kantner, S.S.; Mazurek, M. PMSE Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1982, 14(1), 562-566.
204. Stark, F.O.; Falender, J.R.; Wright, A.P. In Comprehensive Organometallic Chemistry: The Synthesis, Reactions and Structures of Organometallic Compounds; Wilkinson, G.; Stone, F.G.; Abel, E.W., Eds.; Pergamon Press, Oxford, Vol 2, pp. 305-363.
205. Bostik, E.E. In Block Copolymers; Aggerwall, S.L. Ed.; Plenum Press: New York, 1970; pp. 237-247.
206. McGrath, J.E. Riffle, J.S.; Banthia, A.K.; Yilgor, I.; Wilkes, G.L. In Initiation of Polymerization,

- Bailey, F.E., Ed.; ACS Symposium Series Vol.212; American Chemical Society: Washington D.C., 1983,
207. Sigwalt, P. Polym. J. 1987, 19(5), 567-580.
208. Crivello, J.V. Lee, J.L.; Conlon, D.A. In Advances in Elastomers and Rubber Elasticity; Lal, J. and Mark, J.E., Eds.; Plenum Press: New York, 1986, pp. 157-173.
209. Elsbernd, C.S.; Spinu, M.; Kilic, S.; McGrath, J.E. Polymer Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1988, 29(1), 355-357.
210. Frye, C.L.; Salinger, R.M.; Fearon, F.W. J. Org. Chem. 1970, 35, 1308.
211. Riffle, J.S.; Sinai-Zingde, G.; DeSimone, J.D.; Hellstern, A.M.; Chen, D.H.; Yilgor, I. Polymer Prepr. (Am. Chem. Soc. Div. Polym. Sci.) 1988, 29(2), 93--96.
212. Varshney, S.; Beatty, C.L. Org. Coat. Plast. Chem. 1981, 45 152-157.
213. Kazama, H.; Tezuka, Y.; Imai, K. Polym. J. 1987, 19(9), 1091-1100.
214. Speier, J.L. In Advances in Organometallic Chemistry; Ed.; Academic Press: 1979, vol 17, 407-447.
215. Quirk, R.P.; Chen, W.C.; Cheng, P.L. In Reactive Oligomers, Spinelli, H.J. Ed.; ACS Symposium Series, No. 208.; American Chemical Society: Washington DC., 1985, p.139.
216. Williams, E.A. In Annual Reports on NMR Spectroscopy; Academic press: London, 1983, vol. 15, pp. 235-289.
217. Levy, G.C.; Carigioli, J.D. In Nuclear Magnetic Resonance Spectroscopy of Nuclei Other Than Proton; Axenrod, T.; Webb, G.A., Eds.; pp. 251-275.
218. Coleman, B. In NMR of Newly Accessible Nucli; Laszlo, P., Ed.; Academic Press: 1983, vol 12, pp. 197-227.
219. Harris, R.K.; Kimber, B.J. J. Magnetic Resonance 1975, 17, 174-188.

220. Juliano, P.C. U.S. Patent 3 663 650.
221. Shimada, M.; Miyahara, M.; Tahara, H.; Shinohara, I.; Okano, T.; Kataoka, K.; Sakurai, Y. Polym. J. 1983, 15(9), 649-656.
222. Pietrasanta, Y.; Fleury, E.; Boutevin, B.; Sarraf, L. Polym. Bull. 1986 15, 107-112.
223. Bostik, E.E.; Private Communication.
224. Inoue, H.; Kohamas, S.J. J. Appl. Polym. Sci. 1984, 29, 877.
225. Stockmayer, W.H. J. Chem. Phys. 1945, 13, 199.
226. Stejskal, J.; Kratochvil, P. Macromolecules 1987, 20, 2624-2628.
227. Stejskal, J.; Kratochvil, P. Polym. J. 1982, 14(8), 603-627.
228. Stejskal, J.; Kratochvil, P.; Jenkins, A.D. Macromolecules, 1987, 20(1), 181.
229. Poesva, J.; Stejskal, J.; Kratochvil, P. Macromolecules 1987, 20, 2195-2201.
230. Stejskal, J.; Kratochvil, P.; Smith, S.D.; McGrath, J.E. submitted for publication in Macromolecules.
231. Sychaj, T.; Hamielec, A.E. Die Angewandte Makromolekulare Chemie 1988, 157, 137-151.
232. Tung, L.H. In Encyclopedia of Chemical Technology; 3rd ed.; Vol. 7; John Wiley & Sons: New York, 1987, pp. 298-327.
233. Tacx, J.C.J.F.; Ammerdorffer, J.L.; German, A.L. Polymer, 1988, 29, 2087-2094.
234. Mencer, H.J. Polym. Eng. Sci. 1988, 28(8), 497-505.
235. Yilgor, I.; McGrath, J.E.; Krukonis, V.J. Polymer Bull. 1984, 12, 491.
236. McHugh, M.; Krukonis, V.J. Supercritical Fluid Extraction; Principles and Practice; Butterworth: Boston, 1986.

CHAPTER VIII

APPENDIX

APPENDIX 1. PROGRAM TO FOLLOW REACTION PROGRESS. This program was utilized to follow the formation of various ketene silyl acetals as well as PDMS macroinitiator. It permits the collection and storage of a series of FIDs with fixed or variable time intervals between spectra. Programs such as this can be found in NMR data acquisition manuals.

```
1 ZE
2 GO = 2
  acquire data
3 WR FID
  store FID as -----
4 IF FID
5 VD
  wait a delay taken from VD list
6 IN = 1
```

```

increment VD list pointer, loop for next
FID, repeat NE times
7 EXIT

```

Parameters :

- a) Use DS = 4 when not allowing for equilibrium magnetization.
- b) The variable delay (VD) and number experiments (NE) must be set prior to starting the program (Au).
 - 1) VD = list of delays (in sec.) These are the intervals between the end of one acquisition and the beginning of the next.
 - 2) NE = number of VD values and FIDs.

APPENDIX 2. GC METHOD USED TO ANALYZE GTP INITIATOR PURITY. Samples taken during the fractional distillation of GTP initiators were routinely analyzed by GC using a Varian Vista 6000 instrument interfaced with an IBM personal computer .

Single Channel Method:

Section 1: Basic

Page 1: Analysis Parameters

```

Channel 2
Calculation: A†
Area / Ht: A
Stop Time: 20.00 min
Number Expected PKS: 100
Equilibration Time: 0
Unretained PK Time: 0.00
Unident Pk Factor: 0.00
Slice Width: 10

```

Page 2: Sample Parameters

Run Type : A or B

(Analysis or
Baseline)

```

Sample ID:
Divisor: 1.0
Amt std: 1.0
Mltplr: 1.0

```

Page 3: Report Instructions

Where to report: L
 Copies: 1
 Title:
 Format: N
 Decimal place: 4
 Result units:
 Report Unident Pks: Y
 Report Instrument Conditions: Y

Page 4: Plot Instructions

Plot: Y
 Zero Offset: 5
 Annotation:
 Retention Time: N
 Plot Control: Y
 Time Ticks: Y
 Time Events: N
 Pk Start / End: N

Page 5: Chart Speed

Pages or cm/min: C
 Init Value: 1.0

Page 6: Plot Atten

Initial Value: (Select a value)

Section 2: Time Events

Page 1

Line#	Time	Events	Value
1	0.00	PR	100
2	0.00	SN	2
3	0.00	%T	5
4	0.00	WI	15

Section 4: GC Instrument Control

Page 1: Column Temp.

iso/initl Col Temp.: 50
 init Hold Time: 5.00

Step#	Final Temp.	Rate	Hold Time
1	125	5.00	0.00

Page 2: Detectors

Det. A Type: FID
 Det. B Type: ---

Line#	Time	Side	Attn	Range	Zero
1	0.00	A	8	12	Y
2	0.00	B	-	--	N

Page 3: Temp. / Flow
Inj A Temp.: 250
Inj B Temp.: ---
Ion Temp.: 350

**The vita has been removed from
the scanned document**